

Synthesis, Structure, and Stereochemistry of Double-Chain Surfactant Co(III) Complexes

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Double-chain surfactant octahedral Co(III) complexes **1** and **2** ($X = \text{ClO}_4$) (**a**, $R = \text{C}_6\text{H}_{13}$; **b**, $R = \text{C}_8\text{H}_{17}$; **c**, $R = \text{C}_{10}\text{H}_{21}$; **d**, $R = \text{C}_{12}\text{H}_{25}$; **e**, $R = \text{C}_{14}\text{H}_{29}$; **f**, $R = \text{C}_{16}\text{H}_{33}$) were synthesized in H_2O and 20:1 (v/v) EtOH– H_2O by the reaction of $\text{RNHCH}_2\text{CH}_2\text{NH}_2$ (**5**) with $\text{Na}_3\text{Co}(\text{NO}_2)_6$, followed by the addition of NaClO_4 . The cisoid **1**/transoid **2** diastereomer ratio increased upon going from EtOH– H_2O to H_2O , in particular by a factor of ≈ 5 for the octyl and dodecyl systems and ≈ 8 for the hexadecyl system. The increase in the relative amount of cisoid **1** was attributed to the hydrophobic effect associated with the aggregation of ligand **5** in H_2O . Surfactant complexes **3** and **4** ($X = \text{NO}_3$) were also prepared in EtOH(MeOH)– H_2O . The characterization of **1**–**4** included single-crystal X-ray diffraction studies of **1e** and **3a**, measurement of their Krafft temperatures, and demonstration of the cleavable nature of **3a** and **4a**.

Introduction

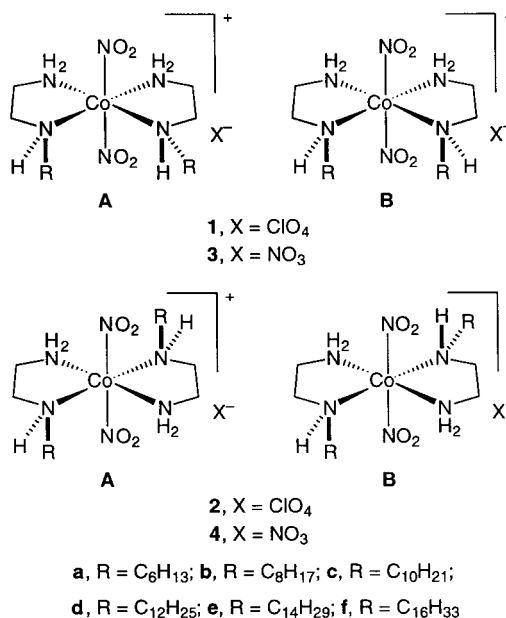
The rich variety of stereochemistry displayed by transition-metal coordination complexes¹ provides the opportunity for the synthesis of derived surfactants with structural and performance characteristics² that are unobtainable with conventional surfactants, which do not contain metals. There are only a few reports³ of the synthesis, isolation, and characterization of surfactant transition-metal complexes, in contrast to numerous reports of the formation and study of such surfactants in solution without isolation.⁴ In part, the number of characterized isolated surfactants is small because the coordination complexes of many first-

row transition-metal ions are labile and the selective synthesis and separation of surfactant stereoisomers can be difficult.

As part of our studies of transition-metal-based surfactants, we have synthesized and determined the structures and stereochemistry of double-chain surfactant octahedral Co(III) complexes **1**–**4**.⁵ Because compounds **1**–**4** are largely insoluble in

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- (1) Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. P., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 1, Chapter 2, p 31.
- (2) Clint, J. H. *Surfactant Aggregation*; Chapman and Hall: New York, 1992.
- (3) For examples, see (a) Muñoz, S.; Gokel, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 4899. (b) Muñoz, S.; Gokel, G. W. *Inorg. Chim. Acta* **1996**, *250*, 59. (c) Fallis, I. A.; Griffiths, P. C.; Griffiths, P. M.; Hibbs, D. E.; Hursthouse, M. B.; Winnngton, A. L. *J. Chem. Soc., Chem. Commun.* **1998**, 665. (d) Iida, M.; Tanase, T.; Asaoka, N.; Nakanishi, A. *Chem. Lett.* **1998**, 1275. (e) Yashiro, M.; Matsumoto, K.; Yoshikawa, S. *Chem. Lett.* **1989**, 985. (f) Yashiro, M.; Matsumoto, K.; Seki, N.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1559. (g) Behm, C. A.; Creaser, I. I.; Korybut-Daszkiewicz, B.; Geue, R. J.; Sargeson, A. M.; Walker, G. W. *J. Chem. Soc., Chem. Commun.* **1993**, 1841. (h) Behm, C. A.; Boreham, P. F. L.; Creaser, I. I.; Korybut-Daszkiewicz, B.; Maddalena, D. J.; Sargeson, A. M.; Snowdon, G. M. *Aust. J. Chem.* **1995**, *48*, 1009. (i) Arumugam, M. N.; Arunachalam, S. *Indian J. Chem.* **1997**, *36A*, 84. (j) Bruce, D. W.; Denby, I. R.; Tiddy, G. J. T.; Watkins, J. M. *J. Mater. Chem.* **1993**, *3*, 911. (k) Menger, F. M.; Lee, J.-J.; Hagen, K. S. *J. Am. Chem. Soc.* **1991**, *113*, 4017. (l) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1997**, *99*, 4947. (m) Sakai, S.; Fuginami, T. *Hyomen* **1990**, *28*, 644, and references therein.
- (4) For examples, see (a) Lu, X.; Zhang, Z.; Liang, Y. *Langmuir* **1997**, *13*, 533. (b) Ghirlanda, G.; Scrimin, P.; Tecilla, P.; Toffoletti, A. *Langmuir* **1998**, *14*, 1646. (c) Hampl, F.; Liska, F.; Mancin, F.; Tecilla, P.; Tonellato, U. *Langmuir* **1999**, *15*, 405. (d) Kofman, V.; Shane, J. J.; Dikanov, S. A.; Bowman, M. K.; Libman, J.; Shanzer, A.; Goldfarb, D. *J. Am. Chem. Soc.* **1995**, *117*, 12771. (e) Bhattacharya, S.; Snehalatha, K.; George, S. K. *J. Org. Chem.* **1998**, *63*, 27, and references therein.



H_2O , even at temperatures of $> 25^\circ\text{C}$ (see below), their practical application as surfactants is limited. On the other hand, it is noteworthy that **1f** and **2f** formed monolayers on a subphase of H_2O at 25°C that are characteristic of H_2O -insoluble surfactants.^{2,5a}

(5) Some of these results have been communicated: (a) Jaeger, D. A.; Reddy, V. B.; Arulsamy, N.; Bohle, D. S.; Grainger, D. W.; Berggren, B. *Langmuir* **1998**, *14*, 2589. (b) Jaeger, D. A.; Reddy, V. B.; Bohle, D. S. *Tetrahedron Lett.* **1999**, *40*, 649.

Experimental Section

General Methods and Materials. ^1H (270 and 400 MHz) NMR spectra were recorded in CDCl_3 and 5:1 $\text{CDCl}_3\text{--CD}_3\text{OD}$ with Me_4Si and CD_2HOD (δ 3.30 relative to Me_4Si) as internal standards, respectively, and ^{13}C (67.9 and 100.6 MHz) NMR spectra in $\text{CDCl}_3/5:1 \text{CDCl}_3\text{--CD}_3\text{OD}$ with CDCl_3 (center line at δ 77.00 relative to Me_4Si) as the internal standard. J values are in hertz. UV-vis spectra were recorded in HPLC-grade MeOH on a Perkin-Elmer Lambda 9 spectrophotometer with quartz cuvettes ($1 \times 1 \times 4.8$ cm). IR spectra of KBr pellets were recorded on a Perkin-Elmer 1600 spectrometer. Magnetic susceptibilities were recorded by the Faraday method on a Johnson Mathey magnetic susceptibility balance (MSB-1) at 25 °C; the magnetic field was calibrated with $\text{Hg}[\text{Co}(\text{SCN})_4]$.⁶ Analytical reversed-phase HPLC was performed with UV detection (254 nm) on a 25-cm \times 4.6-mm (i.d.) C18 column (Rainin 83-201-C) fitted with a 4-cm \times 4.6-mm (i.d.) C8 guard column (Rainin 83-201-G). Eluants were prepared with $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and HPLC-grade MeOH and H_2O . Column chromatography was performed on silica gel (J. T. Baker 3405) and TLC on 0.25-mm silica gel plates (EM 5554-7) with 10:1 $\text{CH}_2\text{Cl}_2\text{--MeOH}$ as the eluant and visualization by 5% (w/v) phosphomolybdic acid in MeOH (ligands) or near-UV irradiation [cobalt(III) surfactants]. Sonication was performed with a Branson 2200 (125-W) ultrasonic cleaner. Extracts were dried over anhydrous Na_2SO_4 . Melting points (decomposition temperatures) were measured with open-end capillary tubes on a Fisher-Johns melting apparatus and are uncorrected. Relative amounts describing solvent mixtures represent relative volumes. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Connolly surface areas and volumes were calculated from the crystallographically determined coordinates using the Cerius 4.2 suite of programs.

***N*-Alkylethylenediamine Ligands 5.** Ligands **5a**⁷ and **5b**–**f**⁸ were prepared by a literature procedure.⁸

Sodium Hexanitrocobaltate(III). This compound was synthesized by a literature procedure.⁹ The oxidation of Co(II) to Co(III) for a sample was verified by measurement of its magnetic susceptibility. When paramagnetic impurities were detected, the product was redissolved in H_2O , and air oxidation was repeated until the conversion of Co(II) to Co(III) was complete.

Surfactant Complexes 1–4. The complexes were prepared from ligands **5** and sodium hexanitrocobaltate(III) by procedures based on that for *trans*-dinitro-bis(ethylenediamine)cobalt(III) nitrate.¹⁰ Aqueous EtOH(MeOH) and H_2O were used as reaction solvents. Detailed procedures are given below for the syntheses of **1** and **2** in 20:1 EtOH– H_2O and H_2O . Satisfactory carbon and hydrogen combustion analyses (± 0.4) were obtained for complexes **1–4**; see Table 1.

***trans*-Dinitro-*cisoid*-bis(*N*-alkylethylenediamine)cobalt(III) Perchlorates (1) and *trans*-Dinitro-*transoid*-bis(*N*-alkylethylenediamine)cobalt(III) Perchlorates (2) in 20:1 EtOH– H_2O .** CAUTION! Perchlorates are potentially explosive. Although we have had no explosions in our work with **1** and **2**, appropriate precautions should be taken in working with them. The following synthesis of **1f** and **2f** is representative. A mixture of 626 mg (2.20 mmol) of powdered **5f** and 100 mL of absolute EtOH was sonicated at 25 °C for 3 min to give a clear solution. Then, a solution of 485 mg (1.20 mmol) of sodium hexanitrocobaltate(III) in 5.0 mL of H_2O at 25 °C was added dropwise for 15 min, after which the reaction mixture was stirred for 2 h at 25 °C. During this time the initially cloudy reaction mixture became clear and yellow-orange. The reaction mixture was rotary evaporated at ≈ 40 °C and the residue dissolved in 75 mL of CH_2Cl_2 . The resultant solution was washed with two 10-mL portions of saturated aqueous NaClO_4 , followed by two 100-mL portions of H_2O , and then it was rotary evaporated. A solution of the residue in 10 mL of CH_2Cl_2 was filtered

Table 1. Carbon and Hydrogen Combustion Analyses for Complexes **1–4**

complex	formula	calcd		found	
		C	H	C	H
1a	$\text{C}_{16}\text{H}_{40}\text{N}_6\text{CoClO}_8$	35.66	7.48	35.80	7.42
2a	$\text{C}_{16}\text{H}_{40}\text{N}_6\text{CoClO}_8$	35.66	7.48	35.58	7.40
1b	$\text{C}_{20}\text{H}_{48}\text{N}_6\text{CoClO}_8 \cdot 0.5\text{H}_2\text{O}^a$	39.77	8.18	39.79	7.91
2b	$\text{C}_{20}\text{H}_{48}\text{N}_6\text{CoClO}_8 \cdot 0.5\text{H}_2\text{O}^a$	39.77	8.18	39.77	7.91
1c	$\text{C}_{24}\text{H}_{56}\text{N}_6\text{CoClO}_8$	44.27	8.67	44.50	8.56
2c	$\text{C}_{24}\text{H}_{56}\text{N}_6\text{CoClO}_8$	44.27	8.67	44.54	8.60
1d	$\text{C}_{28}\text{H}_{64}\text{N}_6\text{CoClO}_8$	47.55	9.12	47.67	9.10
2d	$\text{C}_{28}\text{H}_{64}\text{N}_6\text{CoClO}_8$	47.55	9.12	47.67	9.04
1e	$\text{C}_{32}\text{H}_{72}\text{N}_6\text{CoClO}_8$	50.35	9.51	50.46	9.56
2e	$\text{C}_{32}\text{H}_{72}\text{N}_6\text{CoClO}_8$	50.35	9.51	50.41	9.49
1f	$\text{C}_{36}\text{H}_{80}\text{N}_6\text{CoClO}_8$	52.77	9.84	52.70	9.55
2f	$\text{C}_{36}\text{H}_{80}\text{N}_6\text{CoClO}_8$	52.77	9.84	53.02	9.77
3a	$\text{C}_{16}\text{H}_{40}\text{N}_7\text{CoO}_7$	38.32	8.04	38.18	7.95
4a	$\text{C}_{16}\text{H}_{40}\text{N}_7\text{CoO}_7$	38.32	8.04	38.39	8.04
3b	$\text{C}_{20}\text{H}_{48}\text{N}_7\text{CoO}_7$	43.08	8.68	42.87	8.47
4b	$\text{C}_{20}\text{H}_{48}\text{N}_7\text{CoO}_7$	43.08	8.68	43.36	8.65
3c	$\text{C}_{24}\text{H}_{56}\text{N}_7\text{CoO}_7$	46.97	9.20	46.93	9.11
4c	$\text{C}_{24}\text{H}_{56}\text{N}_7\text{CoO}_7$	46.97	9.20	47.05	9.09
3d	$\text{C}_{28}\text{H}_{64}\text{N}_7\text{CoO}_7$	50.21	9.63	50.07	9.53
4d	$\text{C}_{28}\text{H}_{64}\text{N}_7\text{CoO}_7$	50.21	9.63	50.30	9.65

^a H_2O of crystallization was confirmed by ^1H NMR spectroscopy (CDCl_3).

through a 1.5-cm (i.d.) \times 10-cm column of silica gel packed in CH_2Cl_2 with 1:3 $\text{CH}_2\text{Cl}_2\text{--MeOH}$ as the eluant to remove unreacted starting materials. The residue after rotary evaporation was dried for 2 h (25 °C, 0.1 mmHg) to give crude product that was chromatographed on a 1.5-cm (i.d.) \times 24.5-cm column of silica gel packed in CH_2Cl_2 with CH_2Cl_2 and then $\text{CH}_2\text{Cl}_2\text{--MeOH}$ as the eluant. A pale yellow fraction that contained $< 2\%$ of the crude product eluted with CH_2Cl_2 , followed by 462 mg (51%) of **2f** that eluted with 99:1 to 97:3 $\text{CH}_2\text{Cl}_2\text{--MeOH}$ and 166 mg (18%) of **1f** that eluted with 90:10 to 85:15 $\text{CH}_2\text{Cl}_2\text{--MeOH}$. For **1f**: mp 180 \rightarrow 190 °C (dec); ^1H NMR (270 MHz, CDCl_3) δ 5.12 (br m, 2H), 4.92 (br m, 2H), 4.66 (br m, 2H), 3.07 (br m, 4H), 2.54 (br m, 2H), 2.44 (br m, 6H), 1.94 (br m, 2H), 1.65 (br m, 2H), 1.26 (br m, 52H), 0.88 (t, $J = 6.8$, 6H); ^{13}C NMR (67.9 MHz, CDCl_3) δ 52.74, 52.59, 43.74, 31.93, 29.73, 29.58, 29.37, 29.05, 27.02, 22.69, 14.09; IR 3274 (m), 3235 (w), 3189 (w), 3158 (w), 2924 (s), 2854 (s), 1607 (m), 1467 (s), 1419 (s), 1312 (s), 1281 (w), 1203 (w), 1105 (vs), 1067 (s), 1013 (s), 826 (s), 723 (m), 622 (s) cm^{-1} ; UV-vis λ_{max} 253 nm ($\log \epsilon_{\text{max}}$ 4.35), 350 (3.61), 452 (2.31). For **2f**: mp 180 \rightarrow 190 °C (dec); ^1H NMR (270 MHz, CDCl_3) δ 5.24 (br m, 2H), 5.07 (br m, 2H), 4.77 (br m, 2H), 3.01 (br m, 4H), 2.64 (br m, 4H), 2.44 (br m, 2H), 2.18 (br m, 2H), 1.73 (br m, 4H), 1.25 (br m, 52H), 0.88 (t, $J = 7.0$, 6H); ^{13}C NMR (67.9 MHz, CDCl_3) δ 53.06, 51.62, 43.51, 31.93, 29.74, 29.58, 29.45, 29.37, 28.33, 26.82, 22.69, 14.11; IR 3282 (m), 3235 (m), 3181 (m), 3158 (m), 2924 (s), 2855 (s), 1602 (m), 1466 (s), 1412 (s), 1319 (s), 1271 (m), 1093 (w), 1068 (s), 826 (s), 723 (s), 621 (s) cm^{-1} ; UV-vis λ_{max} 256 nm ($\log \epsilon_{\text{max}}$ 4.41), 353 (3.56), 447 (2.27).

HPLC retention times = 22.4 and 13.2 min for **1f** and **2f**, respectively (eluant = 0.0050 M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ in MeOH; flow rate = 1.0 mL/min).

For **1e**: mp 180 \rightarrow 190 °C (dec); ^1H NMR (400 MHz, CDCl_3) δ 5.14 (br m, 2H), 4.98 (br m, 2H), 4.72 (br m, 2H), 3.10 (br m, 4H), 2.61 (br m, 2H), 2.46 (br m, 6H), 1.95 (br m, 2H), 1.67 (br m, 2H), 1.26 (br m, 44 H), 0.88 (t, $J = 6.8$, 6H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 52.74, 52.63, 43.82, 31.93, 29.73, 29.71, 29.68, 29.59, 29.54, 29.38, 29.36, 29.04, 27.02, 22.70, 14.12; IR 3274 (m), 3235 (m), 3188 (m), 3165 (w), 2929 (s), 2852 (s), 1606 (m), 1464 (s), 1417 (s), 1310 (s), 1279 (m), 1108 (vs), 1062 (s), 1015 (s), 824 (s), 723 (m), 621 (s) cm^{-1} ; UV-vis λ_{max} 253 nm ($\log \epsilon_{\text{max}}$ 4.35), 350 (3.62), 452 (2.32).

1 and 2 in H_2O . The following synthesis of **1f** and **2f** is representative. A mixture of 626 mg (2.20 mmol) of powdered **5f** and 100 mL of H_2O was sonicated at 55 °C for 30 min to give a milky-white emulsion. Then, a solution of 485 mg (1.20 mmol) of sodium hexanitrocobaltate(III) in 5.0 mL of H_2O at 25 °C was added dropwise for 15 min, after which the reaction mixture was stirred for 1 h. The reaction mixture cooled from 55 to 40 °C during the sodium hexani-

- (6) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1958**, 4190.
 (7) Kitamura, T.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1563.
 (8) Linsker, F.; Evans, R. L. *J. Am. Chem. Soc.* **1945**, *67*, 1581.
 (9) Brauer, G. *Handbook of Preparative Inorganic Chemistry*; Academic Press: New York, 1965; Vol. 2, p 1541.
 (10) Holtzclaw, H. F., Jr.; Sheetz, D. P.; McCarty, B. D. *Inorg. Synth.* **1953**, *4*, 176.

trocobaltate(III) addition and to 25 °C by the end of the reaction period. During the reaction, clumps of yellow-orange solid precipitated. The reaction mixture was extracted with 75 mL of CH₂Cl₂, and the extract was washed with two 10-mL portions of saturated aqueous NaClO₄, followed by two 100-mL portions of H₂O, and then it was rotary evaporated to leave crude product. Thereafter, the same procedure as that for the synthesis in 20:1 EtOH–H₂O gave 519 mg (53%) of **1f** and 179 mg (18%) of **2f**.

trans-Dinitro-cisoid-bis(N-alkylethylenediamine)cobalt(III) Nitrates (3) and trans-Dinitro-transoid-bis(N-alkylethylenediamine)-cobalt(III) Nitrates (4) in EtOH(MeOH)–H₂O. The synthesis of **3** and **4** in aqueous EtOH(MeOH) employed the same procedure as that used for **1** and **2** with the substitution of saturated aqueous NaNO₃ for saturated aqueous NaClO₄. For **3d**: mp 180 → 190 °C (dec); ¹H NMR (400 MHz, CDCl₃) δ 5.75 (m, 2H), 5.31 (m, 2H), 5.12 (m, 2H), 3.11 (br m, 2H), 3.02 (br m, 2H), 2.61 (br m, 2H), 2.45 (br m, 6H), 1.93 (br m, 2H), 1.67 (br m, 2H), 1.27 (br m, 36H), 0.88 (t, *J* = 4.6, 6H); ¹³C NMR (100.6 MHz, CDCl₃) δ 52.71, 52.51, 43.53, 31.90, 29.63, 29.54, 29.50, 29.35, 28.99, 26.97, 22.68, 14.12; IR 3254 (m), 3173 (m), 2923 (s), 2852 (s), 1610 (w), 1465 (m), 1412 (s), 1310 (s), 1102 (w), 1019 (m), 823 (s), 721 (w) cm⁻¹; UV–vis λ_{max} 253 nm (log ε_{max} 4.28), 350 (3.55), 449 (2.37). For **4d**: mp 180 → 190 °C (dec); ¹H NMR (400 MHz, CDCl₃) δ 6.47 (m, 2H), 5.50 (m, 2H), 4.73 (m, 2H), 2.99 (br m, 4H), 2.72 (br m, 4H), 2.43 (br m, 2H), 2.13 (br m, 2H), 1.67 (br m, 4H), 1.25 (m, 36H), 0.88 (t, *J* = 7.1, 6H); ¹³C NMR (100.6 MHz, CDCl₃) δ 53.18, 51.51, 43.27, 31.93, 29.70, 29.65, 29.62, 29.57, 29.44, 29.37, 28.24, 27.03, 22.70, 14.14; IR 3255 (m), 3178 (m), 2922 (m), 2854 (m), 1603 (w), 1465 (m), 1420 (m), 1315 (s), 1182 (m), 1022 (m), 824 (s), 721 (w) cm⁻¹; UV–vis λ_{max} 255 nm (log ε_{max} 4.40), 351 (3.58), 445 (2.35).

HPLC retention times = 10.6 and 6.3 min for **3d** and **4d**, respectively (eluant = 0.0040 M NaClO₄·H₂O in 49:1 MeOH–H₂O; flow rate = 1.0 mL/min).

For **3a**: mp 180 → 190 °C (dec); ¹H NMR (400 MHz, CDCl₃) δ 5.41 (br m, 2H), 5.30 (br m, 2H), 5.09 (br m, 2H), 3.09 (br m, 2H), 3.00 (br m, 2H), 2.57 (br m, 2H), 2.45 (br m, 6H), 1.93 (br m, 2H), 1.67 (br m, 2H), 1.32 (br m, 12H), 0.87 (br t, *J* = 6.5, 6H); ¹³C NMR (100.6 MHz, CDCl₃) δ 52.69, 52.57, 43.62, 31.40, 29.16, 26.65, 22.62, 14.07; IR 3260 (s), 3226 (sh), 3185 (s), 2960 (s), 2926 (s), 2863 (s), 1602 (w), 1465 (sh), 1419 (sh), 1377 (vs), 1313 (vs), 1207 (w), 1173 (w), 1100 (m), 1017 (s), 825 (s), 773 (w), 726 (w) cm⁻¹; UV–vis λ_{max} 252 nm (log ε_{max} 4.36), 351 (3.65), 453 (2.38).

Surfactant Complex Stability. Surfactants **1–4** showed no signs of degradation over several months when stored dry and in the dark. But after 3–5 h in contact with dilute sulfuric or hydrochloric acid, a surfactant generally developed a red coloration that was accompanied by decomposition as detected by TLC on silica gel with 10:1 CH₂Cl₂–MeOH as the eluant. Degradation was also observed over a 5-day period in CDCl₃, which can contain acidic impurities.¹¹

Controls on Surfactant Fractionation, Isomerization, and Decomposition. A mixture of 200 mg of **1d** and 100 mg of **2d** was chromatographed on a 1.5-cm (i.d.) × 24.5-cm column of silica gel packed in CH₂Cl₂ with CH₂Cl₂–MeOH as the eluant. Elution with 99:1 to 97:3 CH₂Cl₂–MeOH gave 198 mg of **2d**, followed by 99.8 mg of **1d** with 90:10 to 85:15 CH₂Cl₂–MeOH. Two additional controls gave comparable results. Thus, during column chromatography in their separation and isolation in the above synthetic procedures, the transoid and cisoid isomers do not fractionate, isomerize, or decompose.

Crystallographic Structure Determinations. **1e** and **3a** formed thin, needlelike crystals in MeOH and MeCN, respectively, during slow evaporation (25 °C) over several weeks. Similar crystals were also obtained from slow evaporation of MeCN or MeOH solutions of **3b**, **3c**, and **3e**, but none of them were of diffraction quality. Attempts to grow crystals from **4a–d** under the same conditions gave only thin opaque plates that did not diffract well.

X-ray diffraction data were collected for single crystals of **1e** and **3a** on a Siemens SMART CCD diffractometer equipped with molybdenum radiation, a graphite monochromator, and an LT-2 low-temperature apparatus at 213 K. Cell parameters were obtained from a

Table 2. Crystallographic Data and Refinement Parameters for **1e** and **3a**

	1e	3a
empirical formula	C ₃₂ H ₇₂ ClCoN ₆ O ₈	C ₁₆ H ₄₀ CoN ₇ O ₇
mass (g mol ⁻¹)	763.34	501.48
<i>a</i> (Å)	6.5754(2)	6.6001(13)
<i>b</i> (Å)	10.5182(2)	9.891(2)
<i>c</i> (Å)	30.4789(3)	19.266(4)
α (deg)	98.931(2)	84.83(3)
β (deg)	91.678(2)	80.42(3)
γ (deg)	97.063(2)	85.56(3)
<i>V</i> (Å ³)	2064.09(8)	1232.6(4)
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
temp (°C)	–60	–60
wavelength (Å)	0.71073	0.71073
ρ _{calcd} (g cm ⁻³)	1.228	1.351
abs coeff, μ (mm ⁻¹)	0.531	0.744
R1 ^a	0.1184	0.0652
wR2 ^b	0.2506	0.1500

^a R1 = Σ||F_o| – |F_c||/Σ|F_o|. ^b wR2 = {Σ[w(F_o² – F_c²)]/Σw(F_o²)^{1/2}}^{1/2}, w = 1/[σ²(F_o²) + (kP)²], P = (F_o² + 2F_c²)/3, and k = 0.145 for **1e** and 0.10 for **3a**.

least-squares fit to the angular coordinates of reflections of a series of oscillation frames. Data were measured using ω scans of 0.3° per frame for 30 s, such that a hemisphere was collected. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART^{12a} and refined using SAINT^{12b} on all observed reflections. Data reduction was performed using SAINT, which corrects for Lorentz polarization and decay. The data for **1e**, but not for **3a**, were corrected for absorption using the SADABS program.^{12c} The structures were solved by direct methods and refined by full-matrix least-squares techniques on F² using structure solution programs from the SHELXTL system.¹³

For **3a**, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to nitrogen were located in successive Fourier maps and refined isotropically with fixed positional parameters. All other hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and refined with fixed isotropic thermal parameters set to 1.2 times that of the attached atom. The two hexyl chains are disordered toward their ends; assignment of disordered positions for C(7) and C(8) of one chain and for C(14) of the other gave a satisfactory structure refinement. For **1e**, all non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.96 Å) and refined with fixed isotropic thermal parameters set to 1.2 times that of the attached atom. Crystallographic parameters for **3a** and **1e** are collected in Table 2.

Krafft Temperatures. *T_k* values were determined according to the following procedure, adapted from a literature method.¹⁴ A dispersion of 1.5–2.0 mg of Co(III) complex in 1.0 mL of HPLC-grade H₂O, obtained by brief sonication at 25 °C, was heated until a clear/translucent mixture was obtained. After the mixture was cooled until it became turbid, it was heated at 1 °C/min until it again became clear/translucent. The temperature corresponding to the sharp change to clarity/translucence was recorded as the *T_k* value.

Results and Discussion

Syntheses. The reaction of ligand **5** with Na₃Co(NO₂)₆ in 20:1 EtOH–H₂O or H₂O, followed by the addition of saturated aqueous NaClO₄, gave mixtures of diastereomeric surfactant Co-

(12) (a) SMART Software for the CCD Detector System, Version 4.050; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995. (b) SAINT Software for the CCD Detector System, Version 4.035; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995. (c) Sheldrick, G. M. SADABS Program for Area Detector Absorption Corrections; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(13) Sheldrick, G. M. Crystallographic System, Version 5.03/Iris; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1995.

(14) Démarcq, M.; Dervichian, D. Bull. Soc. Chim. Fr. **1945**, 12, 939.

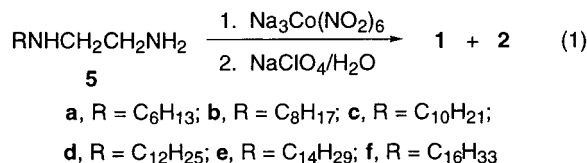
(11) Margolin, Z.; Long, F. A. J. Am. Chem. Soc. **1973**, 95, 2757.

Table 3. Dependence of Cisoid **1**/Transoid **2** Ratios on Reaction Solvent in the Synthesis of **1** and **2**^a

system, R	reaction solvent	% yield 1 + 2 ^{b,c}	1/2 ratio ^c
C ₈ H ₁₇ (b)	20:1 (v/v) EtOH–H ₂ O	67 ± 3	0.38 ± 0.01
C ₁₂ H ₂₅ (d)	20:1 (v/v) EtOH–H ₂ O	64 ± 9	0.36 ± 0.04
C ₁₆ H ₃₃ (f)	20:1 (v/v) EtOH–H ₂ O	66 ± 7	0.36 ± 0.06
C ₈ H ₁₇ (b)	H ₂ O	67 ± 5	2.0 ± 0.2
C ₁₂ H ₂₅ (d)	H ₂ O	69 ± 4	1.9 ± 0.3
C ₁₆ H ₃₃ (f)	H ₂ O	74 ± 3	2.8 ± 0.2

^a See the text for experimental details. ^b Yields for isolated products. ^c The limits of error are average deviations for at least three syntheses.

(III) complexes **1** and **2** (eq 1).¹⁵ The former was in principle

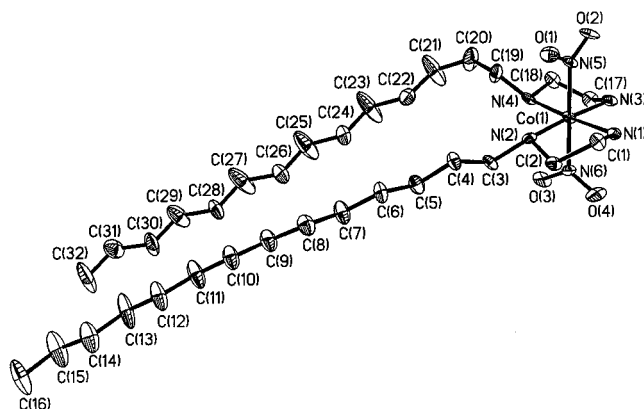


obtained as a mixture of (±)-**1A** (only one enantiomer shown) and *meso*-**1B**, and the latter as a mixture of (±)-**2A** (only one enantiomer shown) and *meso*-**2B**. Analogous complexes **3** and **4** were prepared by the substitution of NaNO₃ for NaClO₄ in the procedure used for **1** and **2**. In each complex the NO₂ groups are trans, and the alkyl groups R are cisoid in **1(3)** and transoid in **2(4)**. Column chromatography on silica gel with CH₂Cl₂–MeOH elution effected separation of **1(3)** and **2(4)** but not of diastereomers **A** and **B** within the cisoid and transoid manifolds. Uniformly, the elution order was the transoid followed by the cisoid manifold. The two manifolds were also separable by reversed-phase (C18) HPLC. As for column chromatography, the elution order was the transoid followed by the cisoid manifold without separation of diastereomers **A** and **B**. Stereoisomers of **1–4** containing *cis*-dinitro groups should be obtainable under different conditions.^{15a,b} Studies of *cis*- and *trans*-dinitrobis(ethylenediamine)cobalt(III) nitrate determined that the latter is the thermodynamic product.^{15a,b}

The ratios of cisoid **1**/transoid **2** obtained in the syntheses displayed a dramatic dependence on the reaction solvent. Uniformly, the **1/2** ratios obtained in H₂O were greater than those obtained in 20:1 EtOH–H₂O. The results are summarized in Table 3 for the octyl (**b**), dodecyl (**d**), and hexadecyl (**f**) systems. On going from 20:1 EtOH–H₂O to H₂O, the **1/2** ratios increased by a factor of ≈5 for the octyl and dodecyl systems and ≈8 for the hexadecyl system. It is unknown whether the **1/2** ratios are kinetically or thermodynamically controlled, although the former is more likely. The origin of the solvent effect in this system, involving the hydrophobic effect associated with the alkyl chains in H₂O, has been discussed previously.^{5a}

Structural Assignments. The structural assignments for **1–4** were based on their IR and ¹H and ¹³C NMR spectra, including ¹H, ¹H and ¹H, ¹³C COSY NMR spectra, and on single-crystal X-ray diffraction studies of **1e** and **3a**. The results of the monolayer study of **1f** and **2f** mentioned above are consistent with the structural assignments.^{5a}

As noted above, **1–4** were in principle obtained as mixtures of diastereomers **A** and **B**. But each of **1–4** gave only one set

**Figure 1.** X-ray structure of **A** of **1e**; ClO₄[−] and hydrogen atoms have been omitted for clarity.

of ¹H and ¹³C NMR signals. Also, comparable ¹H and ¹³C NMR spectra were obtained for all pairs of cisoid **1** and **3** and of transoid **2** and **4**. Assignments for signals in the ¹H and ¹³C NMR spectra of **1b** and **2b** were based on their ¹H, ¹H COSY and ¹H, ¹³C COSY NMR spectra; see the Supporting Information.

The X-ray diffraction results below indicated that the NO₂ groups of **1e** and **3a** are coordinated to Co(III) by nitrogen (nitro ligand) as opposed to oxygen (nitrito ligand). It is known that the IR absorption bands of metal-bound nitro and nitrito groups are different.¹⁶ The IR spectra of **1–4** contained several bands indicating nitro coordination: $\nu_s(\text{NO}_2)$ at ≈1310, $\nu_{as}(\text{NO}_2)$ at ≈1420, and $\delta(\text{NO}_2)$ at ≈824 cm^{−1}. The IR spectra of **1** and **2**, but not of **3** and **4**, displayed a $\rho_w(\text{NO}_2)$ band at ≈622 cm^{−1}.

X-ray Diffraction Studies. Surfactants with long saturated hydrocarbon chains can form crystalline phases,¹⁷ but the obtainment of high-quality single crystals is problematic. Thus, there are relatively few single-crystal X-ray diffraction studies of surfactants.¹⁸ Most of the surfactant complexes **1–4** did not form single crystals suitable for X-ray analysis, although **1** and **3** generally were more crystalline than **2** and **4**; the former two gave needlelike crystals and the latter opaque plates.

The presumed mixtures of stereoisomers **A** and **B** of **1e** and of **3a** resulting from their syntheses were recrystallized from MeOH and MeCN, respectively, to give crystals for single-crystal X-ray diffraction studies. The molecular structures with numbering schemes for **1e** and **3a**, represented as ORTEP plots in Figures 1 and 2, respectively, correspond to **A**.¹⁹ It is unclear whether **A** was formed to the exclusion of **B** in each case or if **A** fractionally crystallized from a mixture of **A** and **B**. An inspection of CPK molecular models of the **A** and **B** stereoisomers of **1(3)** indicated that, at their attachment to nitrogen, the alkyl chains of the latter are sterically more congested than those of the former.

Complexes **1e** and **3a**, lacking an inversion center, crystallized as racemates in the centrosymmetric space group *P* $\bar{1}$ (*Z* = 2). Several other *trans*-dinitro compounds without inversion centers also crystallize in centrosymmetric space groups as racemates.^{19,20} Selected bond lengths and bond angles for **1e** and

(15) Complexes with R = H (NO₃[−] counterion) (**a**, **b**) and R = Me (ClO₄[−], Cl[−], Br[−], and NO₂[−] counterions) (**c**, **d**) have been reported: (a) ref 10. (b) Werner, A. *Justus Liebigs Ann. Chem.* **1912**, 386, 1. (c) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, 89, 3428. (d) Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *Inorg. Chem.* **1968**, 7, 915.

(16) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986.

(17) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 114.

(18) For example, see Jaeger, D. A.; Goodson, P. A.; Arulsamy, N.; Wettstein, J. *Chem. Phys. Lipids* **1998**, 92, 99, and references therein.

(19) Solid-state structures of (±)- and *meso-trans*-dinitro-*transoid*-bis(*N*-methylethylenediamine)cobalt(III) chloride, determined by single-crystal X-ray diffraction, have been reported: Bernal, I.; Cai, J.; Myrczek, J. *Acta Chim. Hung.* **1993**, 130, 555.

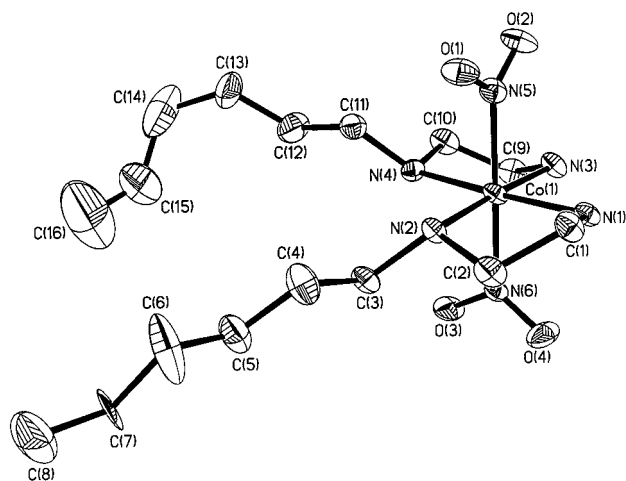


Figure 2. X-ray structure of **A** of **3a**; NO_3^- and hydrogen atoms have been omitted for clarity. Only one of the two positions of atoms C(7), C(8), and C(14) are shown.

3a are given in Table 4. In both **1e** and **3a** the metal center adopts an octahedral geometry with the NO_2 groups occupying the axial positions with Co–N distances of 1.951(6) and 1.932(6) Å for **1e** and 1.960(5) and 1.950(4) Å for **3a**, which are comparable to those of related complexes.^{19,20} The associated N(5)–Co(1)–N(6) bond angles are essentially identical, 179.1(3)° for **1e** and 178.4(2)° for **3a**. The *N*-alkylethylenediamine ligands chelate the Co with the four donor N atoms occupying the equatorial positions with Co–N distances of 1.941(6)–2.023(6) Å for **1e** and 1.937(4)–2.028(4) Å for **3a**, comparable to those of related complexes.^{19,20} The Co–N bonds involving the secondary amino groups are longer than those involving the less nucleophilic primary amino groups, apparently due to steric effects. The N(1)–Co(1)–N(2) plane is tilted with respect to the N(3)–Co(1)–N(4) plane in both **1e** (2.5°) and **3a** (2.1°), but the metal center is in the N(1)–N(2)–N(3)–N(4) plane, with measured deviations of 0.003 and 0.005 Å, respectively. For both complexes the two five-membered chelate rings in one molecule of the unit cell have a δ,δ -conformation, and those in the other have a λ,λ -conformation. These conformations are favored over the alternative δ,λ -conformation by ≈ 1 kcal/mol.^{15d,21} The two alkyl chains extend equatorially from the chelate rings. The cross-sectional areas of **1e** and **3a**'s headgroups are different, 65.28 and 69.16 Å², respectively, likely a result of having different counterions.

The planes defined by the two NO_2 groups are almost orthogonal, with 93.7° and 94.5° angles between them in **1e** and **3a**, respectively. In turn, the NO_2 group planes are almost orthogonal to the N(1)–N(2)–N(3)–N(4) plane in each complex [88.4° and 89.0° for **1e** and 88.7° and 88.1° for **3a** for O(1)–N(5)–O(2) and O(3)–N(6)–O(4), respectively]. Also, viewed along the *z* axis, the O(1)–N(5)–O(2) plane is nearly coplanar with the N(2)–Co(1)–N(3) plane, as is the O(3)–N(6)–O(4) plane with the N(1)–Co(1)–N(4) plane. The O–N–O bond angles and N–O bond distances are comparable

to literature values.^{19,20} In related complexes the NO_2 groups are generally coplanar^{19,20a,b,d,e} or coplanar clavic,^{20b,22} but only occasionally orthogonal.^{19,20c}

In **1e** the NO_2 groups and in **3a** both the NO_2 groups and NO_3^- counterions are involved in intra- and intermolecular hydrogen bonds with amino hydrogens; see the Supporting Information. In particular, each oxygen of the NO_2 groups of both **1e** and **3a** forms an intramolecular hydrogen bond with its nearest amine hydrogen.

Complexes **1e** and **3a** pack in lamellar structures with tail-to-tail arrangements of the alkyl chains as illustrated in Figures 3 and 4, respectively. For **3a**, C(7), C(8), and C(14) were disordered; the final refinements included a site occupancy factor for each of them disordered over two sites. The Co to Co distances across the bilayer and headgroup regions of **1e** and **3a** are 40.233 and 6.944 Å and 15.160 and 7.290 Å, respectively.

The notable differences in the lamellar structures of **1e** and **3a** reflect different packing of their alkyl chains. Both complexes contain one alkyl chain in a near all-trans conformation, C(3)–C(16) for **1e** and C(3)–C(8) for **3a**. The orientations of these chains with respect to the headgroups are defined by Co–N(2)–C(3)–C(4) torsion angles of |156.7|° and |158.9|° for **1e** and **3a**, respectively. The second chain of **1e**, C(19)–C(32), is folded near the headgroup with torsion angles of |112.0|° and |5.8|° for N(4)–C(19)–C(20)–C(21) and C(19)–C(20)–C(21)–C(22), respectively, followed by an all-trans extension to the end of the chain, resulting in a parallel disposition of the two chains and associated interchain London forces. In contrast, the second chain of **3a**, C(11)–C(16), is more extended near the headgroup with torsion angles of |172.6|° and |154|° for N(4)–C(11)–C(12)–C(13) and C(11)–C(12)–C(13)–C(14), respectively, followed by substantial folding at the end of the chain with torsion angles of |56.6|° and |98.8|° for C(12)–C(13)–C(14)–C(15) and C(13)–C(14)–C(15)–C(16), respectively. The torsion angles for Co–N(4)–C(18)–C(19) of **1e** and Co–N(4)–C(11)–C(12) of **3a** are similar, |175.5|° and |167.4|°, respectively, and larger than the corresponding almost identical angles for the near all-trans chains. Thus, the first carbons of the two chains have similar extensions from the headgroup for **1e** and **3a**. Connolly surface area calculations for each alkyl chain in **1e** and **3a** indicate that the chain surface area and volume are larger for the folded chain in each structure (e.g., differences of 11.5 Å² and 12.4 Å³, respectively, for **1e**'s chains). Also, neither structure has any significant void volume among its chains.

Surfactant Characterization. Although the solubility of an ionic surfactant in H_2O generally increases with increasing temperature, it typically increases dramatically at a point known as the Krafft temperature (T_k).² Aggregation of a surfactant can occur only above its T_k value and above its critical aggregation concentration. The surfactant cobalt(III) complexes were characterized by measurement of their T_k values; see the Supporting Information. Surfactants **3a** and **4a** have T_k values of 42 and 38 °C, respectively, and their solubilities in H_2O at 25 °C are 0.0028 (1.4) and 0.0034 M (1.7 mg/mL), respectively. Because the other complexes have T_k values of > 60 °C, their application as surfactants is rendered largely impractical, although solutions of a surfactant below its T_k value, which necessarily contain

(20) (a) Matsumoto, K.; Kuroya, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1755. (b) Bernal, I.; Cetrullo, J. *Inorg. Chim. Acta* **1986**, *122*, 213. (c) Tsuchimoto, M.; Kita, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2554. (d) Börtin, O. *Acta Chem. Scand. A* **1976**, *30*, 657. (e) Shimoi, M.; Fujinawa, Y.; Ogino, H.; Kanamori, K.; Kawai, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3491.
(21) Corey, E. J.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 2620.
(22) (a) Bernal, I. *Inorg. Chim. Acta* **1985**, *101*, 175. (b) Bernal, I.; Schlemper, E. O.; Fair, C. K. *Inorg. Chim. Acta* **1986**, *115*, 25.
(23) Preston, W. C. *J. Phys. Colloid Chem.* **1948**, *52*, 84.

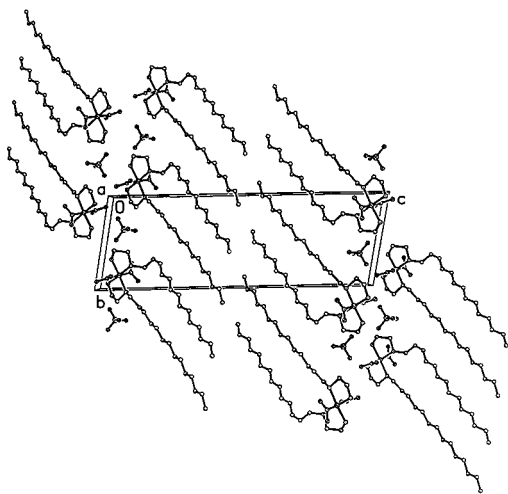
(24) For examples, see (a) Jaeger, D. A. *Supramol. Chem.* **1995**, *5*, 27. (b) Holmberg, K. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 572.
(25) (a) Brown, D. D.; Ingold, C. K.; Nyholm, R. S. *J. Chem. Soc.* **1953**, 2674. (b) Brown, D. D.; Ingold, C. K. *J. Chem. Soc.* **1953**, 2680. (c) Brown, D. D.; Nyholm, R. S. *J. Chem. Soc.* **1953**, 2696.
(26) For example, see Dunkin, I. R.; Gittinger, A.; Sherrington, D. C.; Whittaker, P. *J. Chem. Soc., Chem. Commun.* **1994**, 2245.

Table 4. Selected Bond Lengths and Bond Angles for **1e** and **3a**^a

Bond Lengths (Å)					
	1e	3a		1e	3a
Co(1)–N(1)	1.954(6)	1.967(4)	C(1)–C(2)	1.505(10)	1.498(7)
Co(1)–N(2)	1.985(6)	1.984(4)	N(3)–C[17(9)]	1.488(10)	1.474(7)
Co(1)–N(3)	1.941(6)	1.937(4)	N(4)–C[18(10)]	1.529(9)	1.498(7)
Co(1)–N(4)	2.023(6)	2.028(4)	N(4)–C[19(11)]	1.462(10)	1.486(7)
Co(1)–N(5)	1.951(6)	1.960(5)	C[17(9)]–C[18(10)]	1.481(11)	1.496(8)
Co(1)–N(6)	1.932(6)	1.950(4)	N(5)–O(1)	1.247(8)	1.249(6)
N(1)–C(1)	1.461(9)	1.486(7)	N(5)–O(2)	1.228(7)	1.226(5)
N(2)–C(2)	1.511(9)	1.518(7)	N(6)–O(3)	1.229(7)	1.250(5)
N(2)–C(3)	1.515(9)	1.496(6)	N(6)–O(4)	1.229(8)	1.219(5)

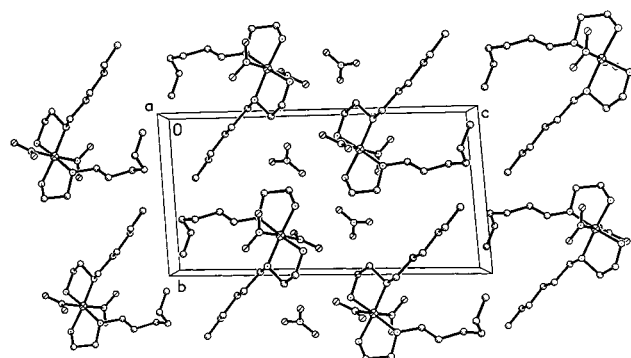
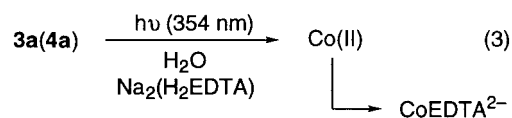
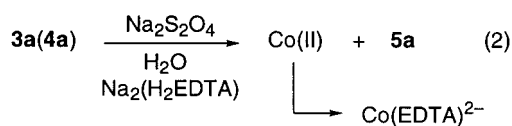
Bond Angles (deg)					
	1e	3a		1e	3a
N(1)–Co(1)–N(2)	85.1(2)	86.3(2)	Co(1)–N(2)–C(2)	108.3(4)	107.6(3)
N(3)–Co(1)–N(4)	85.5(3)	85.8(2)	Co(1)–N(3)–C[17(9)]	110.3(5)	108.9(3)
N(1)–Co(1)–N(3)	91.0(3)	90.3(2)	Co(1)–N(4)–C[18(10)]	106.5(4)	107.3(3)
N(2)–Co(1)–N(4)	98.4(2)	97.6(2)	Co(1)–N(5)–O(1)	120.2(5)	121.1(4)
N(1)–Co(1)–N(4)	176.0(2)	175.9(2)	Co(1)–N(5)–O(2)	119.5(5)	120.7(4)
N(2)–Co(1)–N(3)	175.9(3)	176.1(2)	Co(1)–N(6)–O(3)	120.5(5)	119.6(3)
N(1)–Co(1)–N(5)	88.4(3)	90.1(2)	Co(1)–N(6)–O(4)	121.1(5)	122.6(4)
N(1)–Co(1)–N(6)	90.9(3)	89.7(2)	N(1)–C(1)–C(2)	106.6(2)	107.2(4)
N(2)–Co(1)–N(5)	89.8(3)	89.8(2)	N(2)–C(2)–C(1)	108.2(6)	109.0(4)
N(2)–Co(1)–N(6)	89.7(2)	88.6(2)	N(2)–C(3)–C(4)	113.3(6)	114.6(5)
N(3)–Co(1)–N(5)	91.6(3)	92.0(2)	N(3)–C[17(9)]–C[18(10)]	105.3(6)	107.2(5)
N(3)–Co(1)–N(6)	89.0(3)	89.6(2)	N(4)–C[18(10)]–C[17(9)]	110.0(7)	109.2(4)
N(4)–Co(1)–N(5)	89.8(3)	88.9(2)	N(4)–C[19(11)]–C[20(12)]	116.7(8)	115.2(5)
N(4)–Co(1)–N(6)	91.0(3)	91.4(2)	C(2)–N(2)–C(3)	108.8(6)	109.8(4)
N(5)–Co(1)–N(6)	179.1(3)	178.4(2)	C[18(10)]–N(4)–C[19(11)]	110.8(6)	111.2(4)
O(1)–N(5)–O(2)	120.3(6)	118.1(5)	Co(1)–N(2)–C(3)	121.9(5)	120.2(3)
O(3)–N(6)–O(4)	118.4(6)	117.7(4)	Co(1)–N(4)–C[19(11)]	119.5(5)	119.6(3)
Co(1)–N(1)–C(1)	111.6(5)	110.1(3)			

^a For atoms with two numbers, the first corresponds to **1e** and the second to **3a**.

**Figure 3.** X-ray structure of **A** of **1e** showing the bilayer packing as viewed along the *a* axis.

only monomeric surfactant, display detergency.²³ Additional characterization of the surfactant nature of the cobalt(III) complexes has been reported previously.^{5b}

The cobalt(III) complexes represent cleavable surfactants,²⁴ which can be converted into nonsurfactants or into daughter

**Figure 4.** X-ray structure of **A** of **3a** showing the bilayer packing as viewed along the *a* axis.

surfactants with different aggregation properties, generally by cleavage at a labile functional group. There are only a few examples^{3a,b} of cleavable surfactants based on a transition-metal complex as the labile unit. The stability/labability characteristics of **1–4** derive from the substitutional inertness and lability of Co(III) and Co(II) complexes, respectively.²⁵ Surfactants **3a** and **4a** were cleaved in H₂O containing disodium dihydrogen ethylenediaminetetraacetate [Na₂(H₂EDTA)], by reduction with Na₂S₂O₄ under mild conditions (eq 2) or by irradiation at 354 nm or with sunlight (eq 3), as reported previously.^{5b} Na₂(H₂EDTA) formed a complex with Co(II) and thereby allowed its quantitation as Co(EDTA)²⁻. There have been only a few reports of photocleavable surfactants of any type.²⁶

Summary

Double-chain surfactant Co(III) complex pairs **1** and **2** and **3** and **4** were synthesized. The cisoid **1**/transoid **2** diastereomer ratio increased upon going from EtOH–H₂O to H₂O because of the hydrophobic effect associated with the aggregation of

ligand **5** in H₂O. Single-crystal X-ray diffraction studies of **1e** and **3a** were performed. The Krafft temperatures of **1–4** were determined, and the cleavable nature of **3a** and **4a** was demonstrated.

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Supporting Information Available: Table of Krafft temperatures for complexes **1–4**; tables of selected torsion angles and of hydrogen-bonding distances for **1e** and **3a**; X-ray diffraction results for **1e** and **3a** consisting of tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic parameters, bond lengths and angles, and hydrogen coordinates and isotropic displacement parameters; ¹H,¹H COSY and ¹H,¹³C COSY NMR spectra and structure-¹H and ¹³C NMR chemical shift assignments for **1b** and **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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