STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

SUNDARALINGAM, M. (1969). *Biopolymers*, **7**, 821–860.

SUNDARALINGAM, M. (1973). *Jerusalem Symposium on Quantum Chemistry and Biochemistry*, Vol. V, pp. 417–456. Dordrecht: Reidel.

UMEZAWA, H., SAWA, T., FUKAGAWA, Y., KOYAMA, G., MURASE, M., HAMADA, M. & TAKEUCHI, T. (1965). *J. Antibiot.* A**18**, 178.

WARD, D. C. & REICH, E. (1969). *Ann. Rep. Med. Chem.* **4**, chap. 25.

ZACHARIASEN, W. H. (1968). *Acta Cryst.* A**24**, 212–216.

ZEMLICKA, J. (1975). *J. Amer. Chem. Soc.* **97**, 5896–5903.

Metal Complexes in Detergent Analysis: The Crystal Structure of Bis(ethylenediamine)bis(dodecylsulphato)copper(II)

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Bis(ethylenediamine)bis(dodecylsulphato)copper(II) can be crystallized from absolute ethanol. The crystals are triclinic, space group $P\bar{1}$, $a = 5\cdot608$ (1), $b = 8\cdot247$ (1), $c = 21\cdot381$ (3) Å, $\alpha = 97\cdot30$ (3), $\beta = 95\cdot07$ (3), $\gamma = 104\cdot17$ (3)°, $V = 943\cdot7$ Å^3, $D_m = 1\cdot24$, $D_x = 1\cdot26$ g cm^{-3} for $Z = 1$. The intensities of 4448 unique reflexions were measured with an automatic diffractometer using Mo $K\alpha$ radiation. The structure was solved by standard Fourier methods and refined by full-matrix least-squares methods to a final R of $0\cdot036$ for 2858 reflexions with $I > 3\sigma(I)$. The Cu atom lies on a centre of symmetry. It is planar four-coordinated by the N atoms of two ethylenediamine ligands at a mean distance of $2\cdot007$ (2) Å. Two O atoms of the dodecylsulphato ligands occupy axial positions, $2\cdot517$ (2) Å from the Cu atom. In addition to the Cu—O bond, there are two intramolecular hydrogen bonds from each dodecylsulphato ligand to the bis(ethylenediamine)copper(II) moiety. The dodecyl chains are extended and form a highly ordered interdigitating structure. The non-bonded distances between the C atoms in one dodecyl chain and the closest C atoms in a neighbouring chain are in the range of $4\cdot196$ (5) to $4\cdot301$ (5) Å. The title compound is an example of the complexes formed between detergent anions and the bis(ethylenediamine)copper(II) ion in a recently published method for trace anionic detergent analysis.

Introduction

Analytical methods for the determination of anionic detergents most commonly involve the solvent extraction of an association complex formed between detergent anions and a cationic reagent. The reagent may be either an organic dyestuff such as the methylene-blue cation (*Standard Methods for the Examination of Water and Wastewater*, 1971) or a substitution inert metal chelate such as the tris(1,10-phenanthroline)copper(II) cation (Le Bihan & Courtot-Coupez, 1974). The association complexes formed are of the 'outer-sphere' or 'ion-pair' type first described by Bjerrum (1926). Methods using these reagents are liable to interference from other anions such as chloride and thiocyanate since these can also form extractable association complexes. The bis(ethylenediamine)-copper(II) ion has recently been shown to be a more selective reagent (Crisp, Eckert & Gibson, 1975) and its use has been extended to the analysis of parts per billion concentrations of anionic detergents (Crisp, Eckert, Gibson, Kirkbright & West, 1976).

This paper describes the crystal structure of a complex formed between the bis(ethylenediamine)-copper(II) ion and a typical anionic detergent. Unlike other cations used for detergent analysis, the bis(ethylenediamine)copper(II) ion forms an 'inner-sphere' association complex with detergent anions.

Experimental

Bis(ethylenediamine)bis(dodecylsulphato)copper(II) is precipitated when aqueous solutions of bis(ethylenediamine)copper(II) sulphate and sodium dodecylsulphate (BDH, specially pure) are mixed. Large purple plates were obtained by recrystallization from absolute ethanol.

Preliminary crystal data were obtained with a Supper precession camera using Zr-filtered Mo $K\alpha$ radiation. The Laue symmetry $\bar{1}$ indicated space group $P1$ or $P\bar{1}$. Space group $P\bar{1}$ was confirmed by solution of the structure.

A needle-shaped fragment of a crystal ($0\cdot08 \times 0\cdot12 \times 0\cdot66$ mm) was used for the measurement of intensity

Table 1. *Crystal data for bis(ethylenediamine)bis(do-decylsulphato)copper(II)*

Molecular formula $Cu(H_2NCH_2CH_2NH_2)_2(OSO_2OC_{12}H_{25})_2$
Molecular weight 714·52; m.p. 205°C
Crystal system: triclinic; space group $P\bar{1}$
$a = 5·608\ (1); b = 8·247\ (1); c = 21·381\ (3)$ Å
$\alpha = 97·30\ (3); \beta = 95·07\ (3); \gamma = 104·17\ (3)°$
$V = 943·7$ Å^3; $Z = 1$
$D_m = 1·26; D_x = 1·24$ g cm^{-3}

data. All data were collected on an Enraf–Nonius CAD-4/F automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation [λ(Mo $K\alpha_1$) = 0·70930, λ(Mo $K\alpha_2$) = 0·71359 Å]. The crystal-to-detector distance was 173 mm and the 2θ angle of the monochromator was 12·18°. Unit-cell dimensions were obtained by least-squares refinement of 2θ values for 22 automatically centred reflexions ($\theta > 14°$). A summary of crystal data is given in Table 1. Profile analysis of a representative reflexion indicated that the conditions for the measurement of integrated intensity would be optimized by ω–($\frac{5}{6}$)2θ scans, *i.e.* by scans where the 2θ movement was $\frac{5}{6}$ of the ω movement. Under the optimum conditions the effect of thermal diffuse scattering is minimized by reducing the scan-widths of the reflexions and the horizontal counter aperture as much as possible (Burbank, 1964). The vertical detector aperture was 4 mm and the horizontal aperture was (3·0 + 0·35 tan θ) mm. The ω-scan angle was (0·6 + 0·35 tan θ)°. The scan speeds were determined by a required precision of $\sigma(I) < 0·03I$ with a maximum scan time of 100 s per reflexion. Each reflexion was scanned in 96 steps. The peak, P, was taken to be the 64 central steps, which leaves 16 steps at each end of the scan to measure the backgrounds B_1 and B_2. The intensity (I) was calculated as $I = v[P - 2(B_1 + B_2)]$, where v is a factor to account for differences in the scan speed. The standard deviation in I was defined by the equation $\sigma(I) = \{v[P + 4(B_1 + B_2)]\}^{1/2}$.

Three reference reflexions were measured after every 5000 s of X-ray exposure and the orientation of the crystal was checked after every 200 reflexions. No decomposition or movement of the crystal was detected. The intensities of 4448 independent reflexions ($\theta < 27·5°$) were recorded. 1897 equivalent data ($\bar{h},\bar{k},\bar{l}$) were measured up to $\theta = 20°$.

Lorentz and polarization corrections were applied to the data. The form of the polarization correction (Azaroff, 1955) was $p = (\cos^2 2\theta_m + \cos^2 2\theta)/(1 + \cos^2 2\theta_m)$ where θ_m is the Bragg angle of the mono-chromator crystal, in this case 6·09°. This correction, which is based on the assumption that the graphite monochromator crystal was ideally imperfect, results in a maximum uncertainty of 0·7% in the corrected intensities at $\theta = 30°$ (Mo $K\alpha$ radiation) (Kerr & Ashmore, 1974). Absorption corrections were not

applied since calculations showed that the corrections were not significant [$\mu = 7·3$ cm^{-1} (*International Tables for X-ray Crystallography*, 1974)]. There were 1362 pairs of equivalent reflexions with $I > 3\sigma(I)$. The unweighted discrepancy factor, R_D, defined as ($\Sigma |\Delta F|^2/\Sigma |F_{av}|^2$)$^{1/2}$, was 0·024 where $\Delta F = |F_h| - |F_{\bar{h}}|$ and $F_{av} = (|F_h| + |F_{\bar{h}}|)/2$. An analysis of the errors in the data was made before averaging the two equivalent data sets. A curve was fitted to a plot of mean $[(\Delta F)^2 - \sigma_{stat}^2(F)]$ values *versus* $|F_{av}|$ for the 1362 common observed reflexions in eighteen intervals of $|F_{av}|$, where $\sigma_{stat}^2(F)$ was the statistical variance of the observed structure factor. The data sets were combined and all equivalent data averaged. The value of $\sigma^2(F)$ for each reflexion was recalculated as the sum of $\sigma_{stat}^2(F)$ and the contribution derived from the above curve (Freeman & Guss, 1972). Of the 4448 unique reflexions, only the 2858 with $I > 3\sigma(I)$ were used in the structure analysis.

Structure determination and refinement

The structure was solved by standard Fourier methods and refined anisotropically by full-matrix least-squares

Table 2. *Atomic positional parameters* $(\times 10^4)$ *for bis(ethylenediamine)bis(dodecylsulphato)copper(II)*

Standard deviations are given in parentheses. Hydrogen atoms on calculated positions are not given in the list.

	x	y	z
Cu	0	0	0
S	3354 (1)	−1446 (1)	1192 (3)
O(1)	3602 (3)	−586 (2)	639 (1)
O(2)	1399 (5)	−2967 (2)	1080 (1)
O(3)	5661 (4)	−1588 (4)	1482 (1)
O(4)	2443 (4)	−140 (2)	1665 (1)
N(1)	−828 (5)	1302 (3)	773 (1)
N(2)	2317 (5)	2213 (3)	−88 (1)
C(1)	1976 (6)	−587 (4)	2283 (1)
C(2)	763 (6)	625 (4)	2613 (1)
C(3)	454 (6)	410 (4)	3293 (1)
C(4)	−882 (6)	1562 (4)	3630 (1)
C(5)	−1076 (6)	1425 (4)	4319 (1)
C(6)	−2453 (6)	2560 (4)	4657 (1)
C(7)	−2578 (6)	2463 (4)	5348 (1)
C(8)	−3987 (6)	3561 (4)	5687 (1)
C(9)	−4053 (6)	3480 (4)	6384 (1)
C(10)	−5494 (6)	4551 (4)	6727 (1)
C(11)	−5517 (7)	4475 (5)	7421 (2)
C(12)	−6999 (7)	5496 (5)	7766 (2)
C(13)	281 (8)	3106 (4)	791 (2)
C(14)	2580 (7)	3391 (4)	499 (2)
H(1)	−266 (58)	966 (38)	1080 (14)
H(2)	−2357 (57)	1088 (38)	754 (15)
H(3)	3655 (57)	2090 (38)	−148 (15)
H(4)	1762 (57)	2632 (38)	−392 (14)
H(5)	−809 (58)	3509 (37)	467 (14)
H(6)	481 (53)	3725 (36)	1208 (14)
H(7)	3541 (57)	3039 (39)	818 (15)
H(8)	3412 (54)	4559 (39)	461 (13)

Table 3. *Bond distances* (Å) *and angles* (°) *in bis(ethylenediamine)bis(dodecylsulphato)copper*(II)

Standard deviations are given in parentheses. Superscripts indicate atoms related to those in Table 1 by the following transformations: None x,y,z; (i) $-x,-y,-z$; (ii) $1 - x, -y, -z$; (iii) $x + 1, y, z$.

Cu—N(1)	2·008 (2)	O(2)···H(4ⁱ)	2·29 (3)
Cu—N(2)	2·006 (2)	O(4)···H(1)	2·31 (3)
Cu—O(1)	2·517 (2)	O(1)···H(3ⁱⁱ)	2·43 (3)
S—O(1)	1·455 (2)	O(1)···H(2ⁱⁱⁱ)	2·32 (3)
S—O(2)	1·427 (2)	N(1)—Cu—N(2)	84·9 (1)
S—O(3)	1·422 (2)	N(1)—Cu—O(1)	91·2 (1)
S—O(4)	1·590 (2)	N(2)—Cu—O(1)	86·7 (1)
O(4)—C(1)	1·445 (3)	O(1)—S—O(2)	112·8 (1)
C(1)—C(2)	1·482 (4)	O(1)—S—O(3)	112·8 (1)
C(2)—C(3)	1·507 (4)	O(1)—S—O(4)	101·1 (1)
C(3)—C(4)	1·501 (4)	O(2)—S—O(3)	115·4 (1)
C(4)—C(5)	1·502 (4)	O(2)—S—O(4)	105·9 (1)
C(5)—C(6)	1·508 (4)	O(3)—S—O(4)	107·3 (1)
C(6)—C(7)	1·498 (4)	Cu—O(1)—S	123·3 (1)
C(7)—C(8)	1·501 (4)	S—O(4)—C(1)	117·1 (2)
C(8)—C(9)	1·503 (4)	Cu—N(1)—C(13)	109·3 (2)
C(9)—C(10)	1·504 (4)	Cu—N(2)—C(14)	108·9 (2)
C(10)—C(11)	1·494 (4)	O(4)—C(1)—C(2)	109·2 (2)
C(11)—C(12)	1·495 (5)	C(1)—C(2)—C(3)	114·0 (3)
N(1)—C(13)	1·459 (4)	C(2)—C(3)—C(4)	115·3 (3)
N(2)—C(14)	1·459 (4)	C(3)—C(4)—C(5)	115·7 (3)
C(13)—C(14)	1·462 (5)	C(4)—C(5)—C(6)	115·8 (3)
N(1)—H(1)	0·81 (3)	C(5)—C(6)—C(7)	115·8 (3)
N(1)—H(2)	0·83 (3)	C(6)—C(7)—C(8)	116·4 (3)
N(2)—H(3)	0·80 (3)	C(7)—C(8)—C(9)	115·8 (3)
N(2)—H(4)	0·84 (3)	C(8)—C(9)—C(10)	116·5 (3)
C(13)—H(5)	1·03 (3)	C(9)—C(10)—C(11)	115·9 (3)
C(13)—H(6)	0·95 (3)	C(10)—C(11)—C(12)	116·5 (3)
C(14)—H(7)	0·95 (3)	N(1)—C(12)—C(14)	111·1 (3)
C(14)—H(8)	0·98 (3)	N(2)—C(13)—C(13)	111·3 (3)
		O(2)···H(4ⁱ)—N(2ⁱ)	153 (3)
		O(4)···H(1)—N(1)	157 (3)
		O(1)···H(3ⁱⁱ)—N(2ⁱⁱ)	153 (3)
		O(1)···H(2ⁱⁱⁱ)—N(1ⁱⁱⁱ)	157 (3)

methods. The function minimized was $\Sigma \sigma^{-2}(F)[|F_o| - s|F_c|]^2$, where s is the scale factor. Scattering factors for neutral Cu, S, O, N, C and H together with anomalous dispersion terms for Cu and S were taken from *International Tables for X-ray Crystallography* (1974).

All H atoms were located in difference Fourier maps. However, only the positions of the H atoms of the ethylenediamine ligand were refined. The H atoms of the dodecyl group were placed in their calculated positions [C—H = 0·95 Å (Churchill, 1973)] with the CH_3 group oriented as found in the difference Fourier map. All H atoms were given a fixed isotropic temperature factor ($U_{iso} = 0·063$ Å^2) during refinement. After each refinement cycle the positions of the H atoms on the dodecyl chain were recalculated.

In the final cycles of the refinement all non-hydrogen atoms had anisotropic thermal parameters. A difference Fourier synthesis after the last refinement cycle showed no excursions above background. The final residuals were R (= $\Sigma ||F_o| - s|F_c||/\Sigma |F_o|$) = 0·036, R_w {= $[\Sigma \sigma^{-2}(F)(|F_o| - s|F_c|)^2/\Sigma \sigma^{-2}(F)|F_o|^2]^{1/2}$} =

0·036 for the 2858 reflexions used in the refinement and $R = 0·056$, $R_w = 0·038$ for all 4448 reflexions.

The atomic positional parameters for the non-hydrogen atoms and refined H atoms are listed in Table 2.* The orientation of the terminal CH_3 group is defined by a H atom with coordinates (−0·860, 0·529, 0·753). Selected bond lengths and angles are given in Table 3.

Description of structure and discussion

The Cu atom lies on a centre of symmetry in a tetragonally distorted coordination octahedron. It is planar four-coordinated by the N atoms of two ethylenediamine ligands at a mean distance of 2·007 (2) Å. The axial positions are filled by the O atoms of two dodecylsulphato groups at a distance of 2·517 (2) Å. The mean Cu—N bond distance is within the range found for other bis(ethylenediamine)-copper(II) complexes (Brown & Lingafelter, 1964), and the Cu—O bond distance is slightly less than the values of 2·61 and 2·59 Å found in bis(ethylenediamine)-copper(II) perchlorate (Pajunen, 1967) and bis(ethylenediamine)copper(II) nitrate (Komiyama & Lingafelter, 1964) respectively.

The hydrogen bonds in this structure are weak (Table 3). The NH_2 groups of the ethylenediamine ligand each form one intramolecular and one intermolecular hydrogen bond. The intramolecular hydrogen bonds involve a terminal sulphate O atom [O(2)] and the O atom adjacent to the dodecyl chain [O(4)]. The intermolecular hydrogen bonds are formed between the Cu-bound O atom and the H atoms of the ethylenediamine ligands of a complex related by one unit-cell translation in the x direction (Figs. 1 and 2). The O···H distances and the angles at the H atoms lie within the ranges 2·30 (4)–2·43 (3) Å and 153 (3)–157 (3)°, respectively. No hydrogen bonds are formed by O(3).

The dodecyl chains are extended and lie antiparallel to each other to form a highly ordered interdigitating structure similar to that found in triacetylsphingosine (O'Connell & Pascher, 1969). The average non-bonded distance between a C in one dodecyl chain and the closest C atom in a neighbouring chain is 4·24 Å, with extreme values of 4·196 (5) and 4·301 (5) Å. When viewed along the chain axis, each chain occupies an area of 19·3 Å^2. This is close to the area of approximately 21 Å^2 per molecule calculated from surface tension measurements for the packing of hydrocarbon chains under high pressure at an air–water interface

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* Lists of calculated positions for the hydrogen atoms of the dodecyl chain, structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32657 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
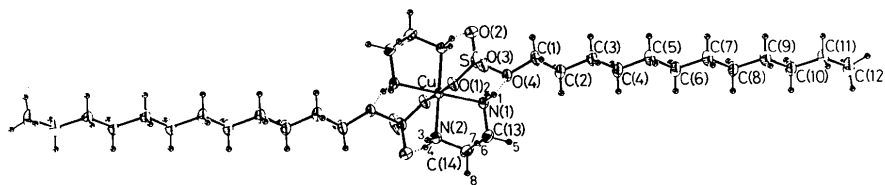
Fig. 1. Bonding arrangement within the bis(ethylenediamine)bis(dodecylsulphato)copper(II) molecule. Refined hydrogen atoms are indicated by small numbers. Dotted lines indicate intramolecular hydrogen bonds.
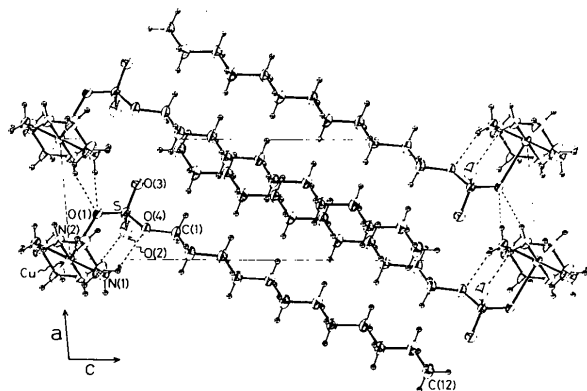

Fig. 2. Packing of bis(ethylenediamine)bis(dodecylsulphato)-copper(II) molecules in the crystal. Projection down b*. Dotted lines indicate hydrogen bonds. For clarity, only those atoms necessary to relate this drawing to Fig. 1 have been labelled.

(Tanford, 1973). The crystal consists of alternating polar layers of $Cu(H_2NCH_2CH_2NH_2)_2(OSO_3)_2$ units interlinked by hydrogen bonds and non-polar layers of perfectly aligned $C_{12}H_{25}$ chains. These layers lie parallel to the xy plane.

Bis(ethylenediamine)bis(dodecylsulphato)copper(II) is an example of the complexes formed between the bis(ethylenediamine)copper(II) ion and alkylsulphate detergents. Alkylbenzenesulphonate detergents should coordinate in a similar fashion since only three of the four O atoms of the dodecylsulphato ligand are involved in coordination or hydrogen bonding and the dimensions of the sulphonato group (Hargreaves, 1957) are comparable to those of the sulphato group.

The 'inner-sphere' association complexes formed between the bis(ethylenediamine)copper(II) ion and detergent anions can be readily extracted into chloroform, but the complexes formed with other potential ligands, such as chloride and thiocyanate, cannot be extracted (Crisp, Eckert & Gibson, 1975; Crisp, Eckert, Gibson, Kirkbright & West, 1976). This, we believe, is because of the strong hydration of any complexes that might be formed with these inorganic anions. The extraction of copper into chloroform only as bis(ethylenediamine)copper(II)–detergent complexes

explains the selectivity of the method for trace anionic detergent analysis employing the bis(ethylenediamine)-copper(II) cation.

References

AZAROFF, L. V. (1955). Acta Cryst. 8, 701–704.
BJERRUM, N. (1926). K. Danske Vidensk. Selsk. Mat. Fys. Medd. 9, 1–48.
BROWN, B. W. & LINGAFELTER, E. C. (1964). Acta Cryst. 17, 254–259.
BURBANK, R. D. (1964). Acta Cryst. 17, 434–442.
CHURCHILL, M. R. (1973). Inorg. Chem. 12, 1213–1214.
CRISP, P. T., ECKERT, J. M. & GIBSON, N. A. (1975). Anal. Chim. Acta, 78, 391–396.
CRISP, P. T., ECKERT, J. M., GIBSON, N. A., KIRKBRIGHT, G. F. & WEST, T. S. (1976). Anal. Chim. Acta, 87, 97–101.
FREEMAN, H. C. & GUSS, J. M. (1972). Acta Cryst. B28, 2090–2096.
HARGREAVES, A. (1957). Acta Cryst. 10, 191–195.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 103–151. Birmingham: Kynoch Press.
KERR, K. A. & ASHMORE, J. P. (1974). Acta Cryst. A30, 176–179.
KOMIYAMA, Y. & LINGAFELTER, E. C. (1964). Acta Cryst. 17, 1145–1148.
LE BIHAN, A. & COURTOT-COUPEZ, J. (1974). Analusis, 2, 695–702.
O'CONNELL, A. M. & PASCHER, I. (1969). Acta Cryst. B25, 2553–2561.
PAJUNEN, A. (1967). Ann. Acad. Sci. Fenn. 138, 2–28.
Standard Methods for the Examination of Water and Wastewater (1971). 13th ed., pp. 339–342. Washington, DC: American Public Health Association.
TANFORD, C. (1973). The Hydrophobic Effect, p. 90. New York: John Wiley.