Os6—Os3—Os2	108.35 (3)	Os4—Os6—Os1	60.68 (3)
Os3—Os4—Os6	60.84 (3)	Os5—Os6—Os3	60.21 (3)
Os3—Os4—Os5	60.11 (3)	Os4—Os6—Os3	58.88 (3)
Os6—Os4—Os5	58.51 (3)	Os1—Os6—Os3	59.50 (3)

An absorption correction based on ψ-scan data was applied, followed by an empirical absorption correction at isotropic convergence (*DIFABS*; Walker & Stuart, 1983). Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1994). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*).

We thank BP Chemicals Ltd for support (JGMN) and the SERC for the provision of a diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Mason, R., Thomas, K. M. & Mingos, D. M. P. (1973). *J. Am. Chem. Soc.* **95**, 3802-3804.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467-473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1994). *Acta Cryst.* In the press.
Stoe & Cie (1988*a*). *DIF*4. *Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988*b*). *REDU*4. *Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158-166.

Acta Cryst. (1994). C**50**, 1054–1057

Sodium Cyclododecyl Sulfate Trihydrate, $Na^+.C_{12}H_{23}O_4S^-.3H_2O$

RAINER RUDERT, DIETER VOLLHARDT
AND GUNTHER CZICHOCKI

Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5, 12484 Berlin, Germany

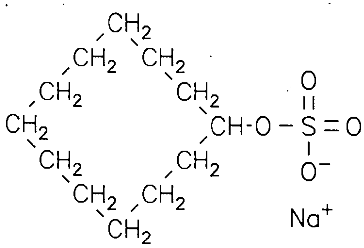
(*Received* 13 *September* 1993; *accepted* 10 *December* 1993)

Abstract

The conformation of the cyclododecyl ring has slightly distorted 422 symmetry. The molecules are packed in a head-to-head arrrangement. The hydrophilic parts of neighbouring molecular layers are connected *via* coordination to Na^+ and hydrogen bonds.

Comment

The continuing interest in the structural analogies of three-dimensional crystals of amphiphiles and their two-dimensional mono- or bilayers is based on comparable intermolecular interactions within the layer planes. In a systematic study of the effect of structural elements there are different possibilities for modifying the amphiphilic nature of a model surfactant, such as sodium dodecyl sulfate. The important role of counter ions in the structural arrangement can be demonstrated by a comparison of the crystal structures of sodium dodecyl sulfate (Sundell, 1977) and butylammonium dodecyl sulfate (Szulzewsky, Schulz & Vollhardt, 1983). However, no systematic information is available on the structural effect of the hydrophobic part of the amphiphilic molecule. Therefore, the long linear hydrocarbon chain of sodium *n*-dodecyl sulfate has been replaced by a large ring hydrocarbon with the same number of C atoms. The asymmetric unit of the title compound, (I), with the atomic numbering scheme is illustrated in Fig. 1.



(I)

As observed previously in different sodium dodecyl sulfate hydrate crystals (Sundell, 1977; Coiro, Mazza & Pochetti, 1986; Coiro, Manigrasso, Mazza & Pochetti, 1987), the three bonds S—O2, S—O3, S—O4 (average length 1.447 Å) are shorter than the ester bond S—O1 [1.571 (4) Å] and the three O—S—O bond angles involving O1 (average bond angle 105.4°) are smaller than the

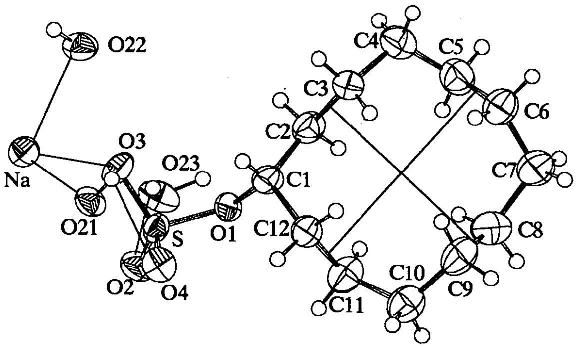


Fig. 1. *PLATON* (Spek, 1990) drawing of the asymmetric unit. The ellipsoids are drawn at the 50% probability level. The two twofold axes of the ring, the $Na^+\cdots O$ coordinations and some of the hydrogen bonds are indicated by thin lines. Three water H atoms could not be determined and are therefore not shown.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

other O—S—O bond angles (average 113.3°). The average C—C bond distance is 1.521 Å and the average C—C—C bond angle is 114.7°.

The cyclododecyl ring has a 422 (D_4) symmetry element which is only slightly distorted. The fourfold axis is perpendicular to the ring plane; the other two twofold axes lie within the plane and connect the midpoints of bonds C2—C3 and C5—C6 with the midpoints of bonds C8—C9 and C11—C12. This conformation is also assumed for the crystal structure of cyclododecane but is uncertain because of poor quality data (Dunitz & Shearer, 1960). Force-field calculations with *MM*2 and *MM*3 (Saunders, 1991) showed that this conformation has the lowest energy of more than 100 different cyclododecane conformers.

As a test of the distortion of the ring symmetry in the title compound, we performed a least-squares fit between the experimental cyclododecyl ring and ideal structures with 422 (D_4) and 222 (D_2) symmetry, varying the atomic positions of the ideal structure without violating the symmetry conditions. The average deviation of C-atom positions between the ideal 422 ring and the experimental structure is 0.112 Å, and between the ideal 222 ring and the experimental structure is 0.025 Å.

The molecules form double layers and are packed in a head-to-head arrangement. In the polar region each Na^+ cation is octahedrally coordinated by four water molecules and two sulfate O atoms with $Na^+\cdots O$ contact distances between 2.330 (5) and 2.483 (5) Å. Na^+ and O3 form an infinite one-dimensional zigzag chain along the *b* axis, connecting both layers. The chains are connected by hydrogen bonds between sulfate O atoms and water molecules and between water molecules, and by $Na^+\cdots$water contacts (see Fig. 2).

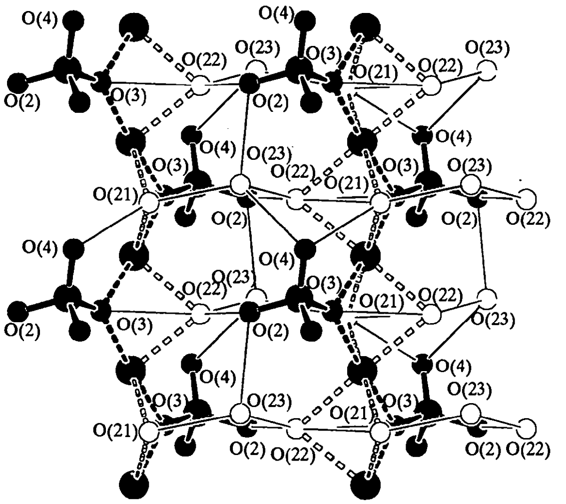


Fig. 2. *SCHAKAL*92 (Keller, 1992) drawing of the intermolecular contacts within the polar region viewed along the direction [001]. Filled circles represent sulfate groups and Na^+ cations, open circles water O atoms, thin lines O···O contacts, open dotted lines $Na^+\cdots O$ contacts and shaded dotted lines $Na^+\cdots O3$ contacts.

The angles between the least-squares plane of the cyclododecyl ring and the *a* and *b* axes are nearly 45°. As a result, the ring planes in adjacent layers are perpendicular to each other (Fig. 3). The two shortest intralayer intermolecular C···C contacts are C3···C11′ and C5···C12′ (Table 3), whose distances are much less than the sum of van der Waals radii of methyl groups (4.2 Å). All interlayer C···C distances are larger than 4 Å. The displacement parameters of the C atoms increase with their distance from the sulfate group, which may reflect the weakness of the intermolecular van der Waals interactions compared to the electrostatic forces in the polar region.

The relatively large amount of water in the crystal makes the crystal structure of the layers comparable with the situation at the water-air interface. The area required by one molecule in each layer is $a \times b = 41.2$ Å^2. At the water-air interface an area per molecule of 56.0 Å^2 has been found (Vollhardt, Czichocki & Rudert, 1993). One reason for this difference may be a dependency of the area per molecule on the number of water molecules per formula unit. Such a dependency has been shown for sodium dodecyl sulfate (Coiro, Manigrasso, Mazza & Pochetti, 1987). A water content of $\frac{1}{8}$, $\frac{1}{2}$ or 1 water molecule(s) per dodecyl sulfate molecule results in an area per molecule of 20.9, 25.8 or 29.5 Å^2, respectively. Another reason may be the higher mobility of the molecules at the surface.

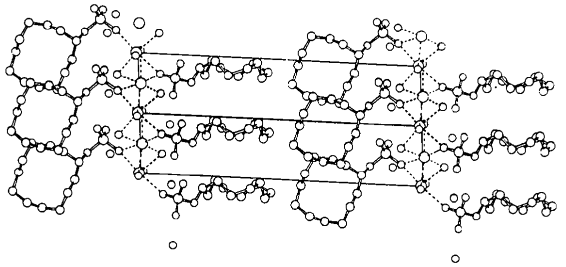


Fig. 3. *SCHAKAL*92 (Keller, 1992) drawing of the molecular packing viewed along the direction [110]. The $Na^+\cdots O$ coordination is indicated by dotted lines. H atoms are not shown.

Experimental

Cyclododecanol (Merck synthesis grade) was purified by recrystallization from acetone and analyzed by gas-liquid chromatography (99.7%). Sodium cyclododecyl sulfate was prepared by sulfation with chlorosulfonic acid (Czichocki, Vollhardt & Seibt, 1981; Vollhardt, Czichocki & Rudert, 1993). The alcohol was dissolved in dimethyl ether at 273 K and treated with 30% excess chlorosulfonic acid (as the dimethyl ether adduct); the reaction mixture was neutralized with 2 *N* sodium carbonate. After cooling, sodium cyclododecyl sulfate was filtered, recrystallized several times from ethyl alcohol and determined by elemental analysis (calculated for $C_{12}H_{23}NaO_4S$, C 50.32, H 8.10, Na 8.03%; found, C 50.00, H 8.13, Na 7.90%). The purity was checked by high-performance liquid chromatography. The residual unchanged cyclododecanol in sodium cyclododecyl sulfate amounts to less than 0.001 mol % (Czichocki & Müller, 1993).

Crystal data

$Na^+.C_{12}H_{23}O_4S^-.3H_2O$
$M_r = 340.42$
Monoclinic
$P2_1$
$a = 6.448$ (3) Å
$b = 6.3940$ (10) Å
$c = 21.392$ (4) Å
$\beta = 95.37$ (3)°
$V = 878.1$ (5) Å^3
$Z = 2$
$D_x = 1.287$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 16$–$20°$
$\mu = 2.08$ mm^{-1}
$T = 300$ K
Plate
0.80 × 0.45 × 0.01 mm
Clear

Data collection

Enraf–Nonius CAD-4 computer-controlled κ-axis diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (ψ scans)
$T_{min} = 0.698$, $T_{max} = 0.998$
1826 measured reflections
1783 independent reflections

1578 observed reflections $[I > \sigma(I)]$
$R_{int} = 0.034$
$\theta_{max} = 70°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = -26 \rightarrow 25$
2 standard reflections
frequency: 30 min
intensity variation: 1.4%

Refinement

Refinement on F
$R = 0.059$
$wR = 0.038$
$S = 3.064$
1541 reflections
190 parameters
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Extinction correction: Zachariasen (1963)
Extinction coefficient: 0.0000043
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S	0.7900 (2)	0.8165 (3)	0.12980 (6)	0.0342 (4)
Na	1.0037 (5)	1.0000	−0.00694 (11)	0.0408 (8)
O1	0.8729 (6)	0.6744 (7)	0.18665 (16)	0.0377 (16)
O2	0.5699 (6)	0.7559 (8)	0.12051 (18)	0.0487 (14)
O3	0.9038 (6)	0.7620 (8)	0.07692 (16)	0.0478 (16)
O4	0.8252 (6)	1.0275 (8)	0.14977 (18)	0.0455 (17)
O21	1.1090 (6)	1.2340 (8)	0.07647 (17)	0.0410 (14)
O22	1.2923 (6)	0.7458 (9)	0.00901 (18)	0.0490 (16)
O23	0.5156 (6)	0.3137 (9)	0.10674 (19)	0.0577 (17)
C1	1.0757 (9)	0.7187 (11)	0.2181 (3)	0.043 (2)
C2	1.1723 (10)	0.5049 (13)	0.2353 (3)	0.048 (2)
C3	1.4062 (10)	0.5162 (13)	0.2618 (3)	0.051 (3)
C4	1.4947 (9)	0.3175 (15)	0.2904 (3)	0.056 (3)
C5	1.4195 (10)	0.2650 (13)	0.3530 (3)	0.063 (3)
C6	1.4907 (11)	0.4075 (13)	0.4069 (3)	0.063 (3)
C7	1.3383 (11)	0.4322 (13)	0.4573 (3)	0.072 (3)
C8	1.1281 (11)	0.5439 (14)	0.4347 (3)	0.073 (3)
C9	1.1505 (10)	0.7719 (14)	0.4199 (3)	0.063 (3)
C10	0.9565 (10)	0.8655 (13)	0.3855 (3)	0.061 (3)
C11	0.9068 (9)	0.7886 (14)	0.3183 (3)	0.055 (3)
C12	1.0591 (9)	0.8595 (11)	0.2730 (3)	0.042 (2)

Table 2. *Selected geometric parameters* (Å, °)

S—O1	1.571 (4)	C4—C5	1.504 (9)
S—O2	1.467 (4)	C5—C6	1.507 (10)
S—O3	1.447 (4)	C6—C7	1.533 (10)
S—O4	1.427 (5)	C7—C8	1.568 (10)
O1—C1	1.442 (7)	C8—C9	1.502 (13)
C1—C2	1.533 (11)	C9—C10	1.514 (10)
C1—C12	1.492 (9)	C10—C11	1.525 (9)
C2—C3	1.562 (9)	C11—C12	1.512 (9)
C3—C4	1.500 (12)		
O1—S—O2	101.9 (2)	C2—C3—C4	115.2 (6)
O1—S—O3	107.8 (2)	C3—C4—C5	114.3 (6)
O1—S—O4	106.4 (2)	C4—C5—C6	116.4 (7)
O2—S—O3	112.7 (2)	C5—C6—C7	115.5 (6)
O2—S—O4	114.5 (3)	C6—C7—C8	115.0 (5)
O3—S—O4	112.6 (3)	C7—C8—C9	114.2 (6)
S—O1—C1	118.4 (4)	C8—C9—C10	113.3 (6)
O1—C1—C2	105.5 (5)	C9—C10—C11	115.0 (6)
O1—C1—C12	110.9 (5)	C10—C11—C12	114.6 (6)
C2—C1—C12	114.0 (5)	C1—C12—C11	115.0 (6)
C1—C2—C3	113.7 (6)		

Table 3. *Contact distances* (Å)

Na—O3	2.483 (5)	O3—O22	3.013 (6)
Na—O21	2.378 (5)	O4—O21	2.844 (6)
Na—O22	2.470 (5)	O4—O23^{iii}	2.800 (7)
Na—O21^{i}	2.330 (5)	O21—O22^{ii}	3.026 (6)
Na—O3^{ii}	2.360 (5)	O21—O23^{iv}	2.690 (6)
Na—O22^{ii}	2.470 (5)	O22—O23^{ii}	2.903 (6)
O2—O22	2.846 (6)	C3—C11^{v}	3.77 (1)
O2—O23	2.861 (8)	C5—C12^{vi}	3.78 (1)

Symmetry codes: (i) $2-x, y-\frac{1}{2}, -z$; (ii) $2-x, \frac{1}{2}+y, -z$; (iii) $x, 1+y, z$; (iv) $1+x, 1+y, z$; (v) $1+x, y, z$; (vi) $x, y-1, z$.

By evaporation of an ethanol solution two kinds of monoclinic crystals, presumably with different water contents, could be grown. The first kind (cell constants $a = 10.65$, $b = 42.1$, $c = 8.17$ Å, $\beta = 92.1°$) degraded quickly during X-ray measurements, therefore the second kind was chosen for the structure determination. H atoms of the title compound were placed in calculated positions (C—H = 0.95 Å) with isotropic displacement parameters set equal those of the parent C atoms. Some H-atom positions of the water molecules were found by difference Fourier synthesis; the isotropic displacement parameter of each was set equal that of the parent O atom. All H-atom parameters were kept fixed during further refinement. Data collection and cell refinement were performed with *CAD*-4 *Software* (Enraf-Nonius, 1989). Data reduction, structure solution and structure refinement were performed using *MolEN* (Fair, 1990). Molecular graphics were prepared using *SCHAKAL*92 (Keller, 1992) and *PLATON* (Spek, 1990). The material for publication was prepared using *PLATON*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Coiro, V. M., Manigrasso, M., Mazza, F. & Pochetti, G. (1987). *Acta Cryst.* **C43**, 850-854.

Coiro, V. M., Mazza, F. & Pochetti, G. (1986). *Acta Cryst.* **C42**, 991-995.

Czichocki, G. & Müller, P. (1993). Unpublished.

Czichocki, G., Vollhardt, D. & Seibt, H. (1981). *Tenside*, **18**, 320-327.

Dunitz, J. D. & Shearer, H. M. M. (1960). *Helv. Chim. Acta*, **43**, 18-35.
Enraf-Nonius (1989). *CAD-4 Software*. Enraf-Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
Keller, E. (1992). *SCHAKAL92. A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
Saunders, M. (1991). *J. Comput. Chem.* **12**, 645-663.
Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
Sundell, S. (1977). *Acta Chem. Scand. Ser. A*, **31**, 799-807.
Szulzewsky, K., Schulz, B. & Vollhardt, D. (1983). *Cryst. Res. Technol.* **18**, 1003-1008.
Vollhardt, D., Czichocki, G. & Rudert, R. (1993). *Colloids Surf.* **A76**, 217-225.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139-1144.

Acta Cryst. (1994). C**50**, 1057–1059

A Palladium–Dithiooxamide Complex

M. Abboudi and A. Mosset

CEMES-LOE, 29 rue J. Marvig,
F31055 Toulouse CEDEX, France

(*Received* 24 *June* 1993; *accepted* 24 *November* 1993)

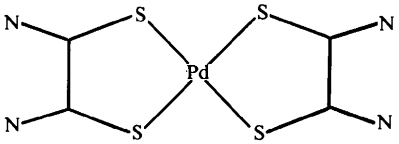
Abstract

Single crystals of bis[dithiooxamido(1−)-*S*,*S*′]-palladium 0.5-methanol solvate 0.5-hydrate, $[Pd(C_2H_3N_2S_2)_2].0.5CH_3OH.0.5H_2O$, are obtained from a methanolic solution of K_2PdCl_6 and dithiooxamide. This complex crystallizes in the monoclinic system (space group *I*2/*a*). The structure can be described as an array of neutral centrosymmetric $Pd(LH_3)_2$ molecules (where $LH_3 = C_2H_3N_2S_2$). Each Pd atom has a near perfect square-planar environment of S atoms. The unsubstituted dithiooxamide molecules are planar and show a *cis* conformation which is observed for the first time in a crystal structure. The methanol molecule is disordered.

Comment

The unsubstituted dithiooxamide ligand $(NH_2)SCCS(NH_2)$, abbreviated to LH_4, forms metallic complexes with almost all *d*-block transition metals and also with some metals from the *p* block, like Sb, Pb or Bi. However, because of the extremely low solubility of these complexes, it is very difficult to obtain suitable single crystals. A small number of crystallographic studies proved the ligand to be in a *trans* conformation (Mosset, Abboudi & Galy, 1983; Belicchi, Ferrari, Pellizzi & Tarasconi, 1985), but many spectroscopic studies indicate the possibility of a *cis* conformation, particularly with Pd (Hofmans, Desseyn, Aarts & Herman, 1982; Bellaihou, Weyten & Desseyn, 1990).

The structure of the title compound consists of an array of two independent $Pd(LH_3)_2$ neutral molecules, situated on a centre of symmetry, and solvent molecules (one molecule of water and a disordered molecule of methanol). Around each Pd atom there exists a near perfect square plane involving four S atoms from two ligands, with a mean Pd—S bond length of 2.267 Å (Fig. 1). This characteristic proves that Pd^{IV} has been reduced to Pd^{II}. Indeed, all complexes in the IV oxidation state which have been studied are octahedral with the low-spin t_{2g}^6 configuration (Greenwood & Earnshaw, 1986). This reduction is not very surprising as Pd^{IV} complexes are rather sparse and much less stable than those of Pd^{II}.



$Pd(LH_3)_2$

Perpendicular to this coordination plane, the apical positions are occupied by two other S atoms; they are situated at distances of 3.61 (1) Å for Pd(1) and 3.67 (1) Å for Pd(2). These distances are extremely long and much greater than the sum of the contact radii. However, these very weak interactions lead to a stacking along [010], at distances shorter than the *b* parameter (Fig. 2). The $Pd(LH_3)_2$ molecules are also held together through hydrogen bonding between O atoms from solvent molecules and amino groups (Table 3).

The most important feature in this structure is the *cis* conformation of the ligand. This is the first time that this conformation, predicted from IR studies, is observed in a crystal structure for the unsubstituted ligand. Thus, the ligand is *S*,*S*′ coordinated to the metal atoms. This situation has already been encountered in Pd complexes with dibenzyl- and dicyclohexyldithiooxamide (Antolini, Fabretti, Franchini, Menabue & Pellacani, 1987). In these three Pd complexes, bond lengths are within the same expected ranges: 2.26–2.30 Å for Pd—S, 1.66–1.74 Å for C—S and 1.28–1.32 Å for C—N. Compared to the free ligand (Wheatley, 1965), the lengthening of the C—S and the shortening of the C—N bonds appear negligible. Torsion angles for S atoms (S—C—C—S) are roughly equal to zero [2 (4) and 4 (4)° in this work, compared to 0.8 and 2.7° for the other Pd complexes]. The dithiooxamide molecules are probably strictly planar, the torsion angles N—C—C—N being equal to 3 (4)°.

Acta Crystallographica Section C
ISSN 0108-2701 © 1994