

length than in bis(2-dimethylaminopyridine 1-oxide)-copper diperchlorate [2.052 (2) Å] or dinitrato-(*N,N,N',N'*-tetramethylethylenediamine)copper(II) [2.003 (2) Å] (Pavkovic, Miller & Brown, 1977). The Cu—O(1) (*N*-oxide oxygen) bonding distance is about the same as in the dimethyl complex, but shorter than in picolinato *N*-oxide and nicotinato *N*-oxide Cu complexes. The N(1)—O(1) distances in the coordinated compounds are in the range 1.330–1.352 Å (Knuuttila, 1983; Knuuttila, 1982), whereas uncoordinated N—O is only 1.314 Å (Knuuttila & Knuuttila, 1983). Coordination suppresses the double-bond character of N—O when the steric conditions are favorable.

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Crystal Phases Obtained from Aqueous Solutions of Sodium Dodecyl Sulfate. The Structure of a Monoclinic Phase of Sodium Dodecyl Sulfate Hemihydrate

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Abstract. $\text{Na}^+\cdot\text{C}_{12}\text{H}_{25}\text{SO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$, $M_r=297.4$, monoclinic, C_2 , $a=9.847(1)$, $b=5.248(1)$, $c=30.798(6)$ Å, $\beta=91.29(1)^\circ$, $V=1591.1(5)$ Å³, $Z=4$, $D_x=1.24$ g cm⁻³, $\lambda(\text{Cu K}\alpha)=1.5418$ Å, $\mu=2.1$ mm⁻¹, $F(000)=644$, $T=285\text{--}288$ K, $R=0.073$ for 1387 observed reflections. This analysis has been carried out since crystal phases which are grown from aqueous micellar solutions can contain structural features common to micelles. The sodium dodecyl sulfate (SDS) molecules are arranged in the crystal to form a lamellar structure with layers alternately polar and apolar. In the polar region the sulfate groups are held together by sodium ions and water molecules through strong ionic interactions and hydrogen bonds. Very weak van der Waals interactions are present in the apolar region. By comparison of this structure with another crystal phase of SDS containing less water, obtained from organic solvent, it emerges that the

lamellar size decreases with increasing surface area of the polar head.

Introduction. Many important aspects of micellar systems such as shape, size and water content of their interior are not yet clear (Dill, Koppel, Cantor, Dill, Bendedouch & Chen, 1984; Menger & Doll, 1984). Therefore, the knowledge of the surfactant structure and aggregation modes in the solid phase is important, in order to obtain models to use in the study of micellar solutions.

SDS forms micellar aggregates in aqueous solution at concentrations over the critical micellar concentration [8.1×10^{-3} mol dm⁻³ (Mukerjee & Mysels, 1971)]. The SDS anion is amphiphilic since it possesses the sulfate group as polar head and the nonpolar hydrocarbon chain ending with a methyl group. A structure determination of SDS has already been made on crystals grown from organic solvent [chloroform-methanol mixture, 9:1 *v:v* (Sundell, 1977)]. In spite of the poor atomic resolution, especially for some carbon

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Table 1. Final fractional coordinates and B_{eq} values for the non-H atoms with e.s.d.'s in parentheses
$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i \cdot a_j$$

| | <i>x</i> | <i>y</i> | <i>z</i> | $B_{eq}(\text{\AA}^2)$ |
|-------|--------------|--------------|-------------|------------------------|
| S(1) | 0.6975 (2) | 0.6835 (16) | 0.0707 (1) | 3.2 (1) |
| Na(1) | 0.6174 (3) | 0.7372 (16) | -0.0375 (1) | 3.8 (1) |
| O(1) | 0.5907 (5) | 0.7136 (20) | 0.1075 (2) | 4.0 (2) |
| O(2) | 0.6238 (6) | 0.5581 (19) | 0.0349 (2) | 4.3 (3) |
| O(3) | 0.8093 (5) | 0.5349 (20) | 0.0873 (2) | 3.9 (2) |
| O(4) | 0.7296 (6) | 0.9449 (19) | 0.0609 (2) | 4.1 (3) |
| C(1) | 0.5568 (8) | 0.4805 (23) | 0.1317 (3) | 3.8 (3) |
| C(2) | 0.4393 (7) | 0.5489 (22) | 0.1605 (3) | 3.7 (3) |
| C(3) | 0.3999 (8) | 0.3335 (25) | 0.1901 (3) | 3.9 (3) |
| C(4) | 0.2791 (8) | 0.4007 (25) | 0.2184 (3) | 4.3 (4) |
| C(5) | 0.2394 (8) | 0.1963 (28) | 0.2499 (3) | 4.4 (4) |
| C(6) | 0.1199 (9) | 0.2700 (26) | 0.2779 (3) | 4.7 (4) |
| C(7) | 0.0796 (9) | 0.0677 (26) | 0.3101 (3) | 4.8 (4) |
| C(8) | -0.0420 (9) | 0.1435 (26) | 0.3378 (3) | 4.7 (4) |
| C(9) | -0.0798 (10) | -0.0571 (29) | 0.3712 (3) | 5.4 (5) |
| C(10) | -0.2015 (10) | 0.0240 (29) | 0.3981 (3) | 5.7 (5) |
| C(11) | -0.2362 (12) | -0.1705 (38) | 0.4324 (4) | 7.9 (7) |
| C(12) | -0.3610 (12) | -0.0949 (47) | 0.4582 (4) | 9.0 (9) |
| O(5) | 0.5000 | 0.0717* | 0.0000 | 3.6 (3) |

* This coordinate was held fixed during the refinement.

atoms of the hydrocarbon chains, some consideration of the crystal packing is possible. In this case the molecules are arranged tail to tail in double layers; the chains are fully extended and almost perpendicular to the polar-head plane.

Hoping to give a contribution to the understanding of the molecular organization of the micellar aggregates we have undertaken the structural elucidation of those crystalline phases which can be grown from SDS aqueous solutions at different concentrations and temperatures.

Experimental. SDS purchased from Sigma Chemical Co. Single crystals in the form of colourless plates obtained by dissolving SDS in water (24 wt%) within temperature range 285–288 K. Approximate unit-cell dimensions and space group determined from oscillation and Weissenberg photographs. Crystal $0.03 \times 0.2 \times 0.6$ mm mounted on automatic Syntex $P2_1$ diffractometer equipped with graphite monochromator and Cu $K\alpha$ radiation. Unit-cell parameters determined from least-squares fit of angular settings of 15 reflections in range $5 < \theta < 20^\circ$. Intensities of 2569 reflections measured, 1387 independent with $I > 1.5\sigma(I)$, $R_{int} = 0.06$, collected by ω -scan technique up to max. 2θ of 130° with scan rate varying in interval $29.3\text{--}2.0^\circ \text{ min}^{-1}$ over scan range 1.2° of ω . Background counts taken for time equal to one third of scan. Three standard reflections (003, 200, 204) measured after every 100 showed steady decrease. This was taken into account to scale intensities which were corrected for Lorentz and polarization factors and for anisotropy of absorption using ϕ -scan curves obtained for two reflections (max., min. correction 2.21, 1.00). No

correction for extinction. Structure solved by interpretation of a sharpened Patterson map which revealed S atom position. Successive Fourier syntheses allowed location of all heavy atoms, refined isotropically and then anisotropically by block-diagonal least squares. Function minimized $\sum w(|F_o| - |F_c|)^2$, $w = (a + |F_o| + c|F_o|^2)^{-1}$, a and c equal to $2F_{o(\min)}$ and $2/F_{o(\max)}$ respectively. Although most H atoms could be detected from difference Fourier synthesis, they were placed at expected positions with isotropic thermal parameters deduced from carrier atoms and held fixed in last cycles of refinement. Atomic scattering factor of S corrected for anomalous dispersion. In final refinement cycle $(\Delta/\sigma)_{\max} = 0.09$ for positional and thermal parameters. Min. and max. heights in final difference Fourier map are -0.2 and 0.5 e \AA^{-3} respectively. Final R and wR are 0.073 and 0.108 respectively and $S = 0.7$. Poor quality of crystals prevented better agreement indices. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations carried out on HP 1000/F minicomputer (Cerrini & Spagna, 1977) of the CNR Research Area.

The final atomic parameters are given in Table 1.*

Discussion. The geometry found for the SDS anion is given in Fig. 1: the average C–C bond length is $1.522(15) \text{ \AA}$ and the average C–C–C valence angle is $113.2(11)^\circ$. The S(1)–O(1) bond length is significantly longer than the other S–O bond lengths, which are similar within the experimental errors; furthermore the other O–S–O valence angles are significantly larger than those including O(1): both these effects may be caused by the negative charge shared among the three oxygens O(2), O(3) and O(4). The conformation of the hydrocarbon chain is completely *trans*: the largest deviation being $2.4(7)^\circ$ for the C(2)–C(3)–C(4)–C(5) torsion angle.

A view of the crystal packing on the *ac* plane is shown in Fig. 2. The molecules are arranged in a lamellar structure with layers alternatively polar and apolar. The SDS chains are arranged tail to tail and the hydrocarbon chain is tilted to the *ac* plane by an angle of $14.7(9)^\circ$. In the polar region structural aggregates are recognizable, each formed by a water molecule, lying on a special position on the twofold axis, surrounded by two sodium ions and two sulfate groups: these aggregates, related by the twofold screw axes, constitute the polar region and cause all adjacent polar heads, sodium ions and water molecules to be aligned along the *a* direction, up and down along *b*.

* Lists of structure factors, anisotropic thermal parameters of the non-H atoms and torsion angles, in agreement with the convention of Klyne & Prelog (1960), have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42894 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The interactions of the Na⁺ ion with the O atoms of the polar heads and the water molecule are shown in Fig. 3.

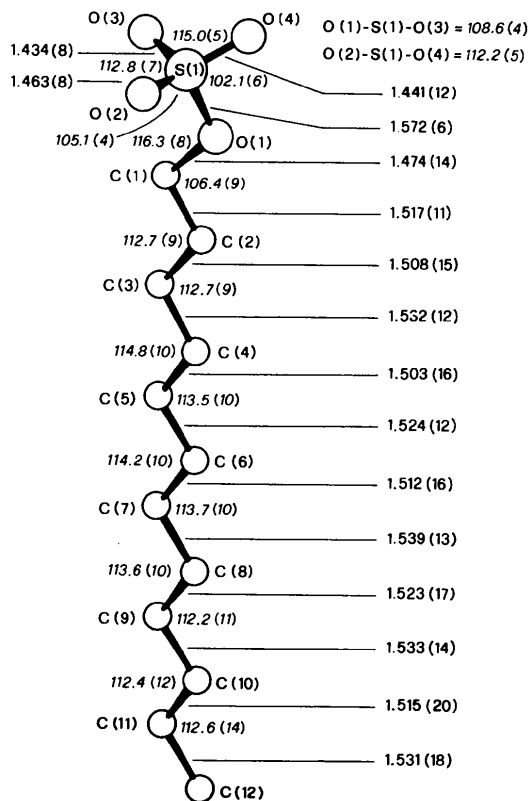


Fig. 1. Atomic numbering, valence bond lengths (Å) and angles (°) found for the SDS anion. E.s.d.'s are given in parentheses.

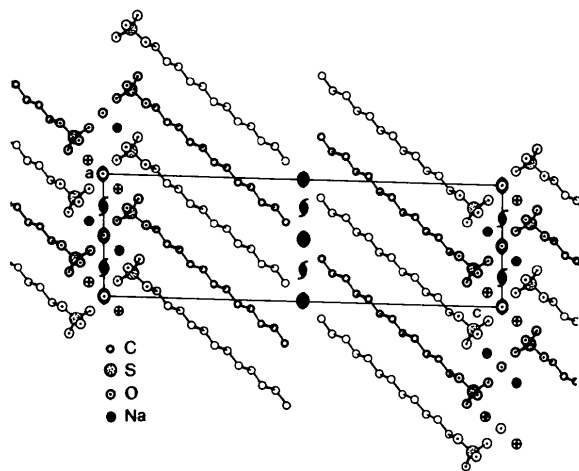


Fig. 2. A view of the crystal packing projected on the *ac* plane. Thick and thin bonds represent molecules at higher and lower heights respectively along *b*.

The sulfate groups are aligned in rows along the *b* direction: in these rows adjacent polar heads are screw-related, while alternating polar heads are related by translation; the two facing rows of polar heads are related by a twofold axis, parallel to *b*, passing through O(5ⁱ). Each Na⁺ ion makes five contacts, ranging from 2.278 (10) to 2.558 (8) Å, with four O atoms of three different polar heads and the O atom of the water molecule; two other longer contacts, 2.943 (6) and 3.054 (9) Å, involving two O atoms of two sulfate groups, are present. The distance between the twofold-symmetry-related Na⁺ ions is 3.306 (4) Å. The angles O...Na...O occurring around the sodium ion are reported in Table 2.

The contacts that the water oxygen makes with the surrounding oxygens of the polar heads are shown in Fig. 4. The relevant angles involving O(5) are given in Table 3. It has not been possible to locate the H atoms;

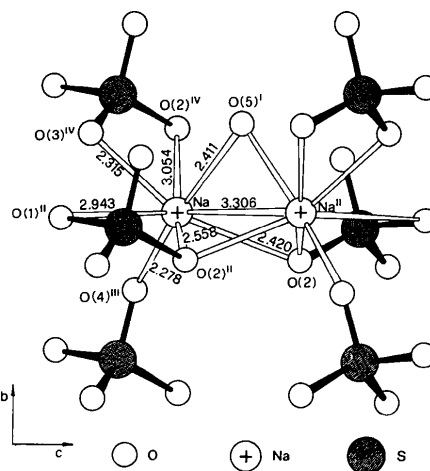


Fig. 3. The interactions that the sodium ion forms with the surrounding atoms. E.s.d.'s are in the range 0.006–0.010 Å and 0.004 Å for the Na...Na contact. The symmetry code is the same as that shown in Table 2.

Table 2. The O...Na...O angles (°) occurring around the sodium ion

E.s.d.'s are in the range 0.2–0.4°.

| | | | |
|---|-------|---|-------|
| O(1 ⁱⁱ)...Na...O(2) | 131.4 | O(2 ^{iv})...Na...O(3 ^{iv}) | 51.2 |
| O(1 ⁱⁱ)...Na...O(2 ⁱⁱ) | 51.4 | O(2)...Na...O(4 ⁱⁱⁱ) | 91.5 |
| O(1 ⁱⁱ)...Na...O(2 ^{iv}) | 127.5 | O(2 ^{iv})...Na...O(4 ⁱⁱⁱ) | 112.6 |
| O(1 ⁱⁱ)...Na...O(3 ^{iv}) | 76.4 | O(2 ^{iv})...Na...O(4 ⁱⁱⁱ) | 79.8 |
| O(1 ⁱⁱ)...Na...O(4 ⁱⁱⁱ) | 101.2 | O(2)...Na...O(5 ⁱ) | 81.0 |
| O(1 ⁱⁱ)...Na...O(5 ⁱ) | 92.8 | O(2 ^{iv})...Na...O(5 ⁱ) | 78.3 |
| O(2)...Na...O(2 ⁱⁱ) | 80.4 | O(2 ^{iv})...Na...O(5 ⁱ) | 89.7 |
| O(2)...Na...O(2 ^{iv}) | 100.7 | O(3 ^{iv})...Na...O(4 ⁱⁱⁱ) | 91.6 |
| O(2 ^{iv})...Na...O(2 ^{iv}) | 167.6 | O(3 ^{iv})...Na...O(5 ⁱ) | 89.2 |
| O(2)...Na...O(3 ^{iv}) | 150.5 | O(4 ⁱⁱⁱ)...Na...O(5 ⁱ) | 165.8 |
| O(2 ⁱⁱ)...Na...O(3 ^{iv}) | 124.9 | | |

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

however, in view of the O...O interactions, they could be in two different positions. In the first, the water could form two bifurcated hydrogen bonds with the two twofold-symmetry-related pairs of atoms O(2), O(4ⁱ) and O(2ⁱⁱ), O(4ⁱⁱⁱ) respectively. In fact, if the hydrogens are assumed to be in the plane of O(2), O(4ⁱ), O(5) and O(2ⁱⁱ), O(4ⁱⁱⁱ), O(5) respectively, at 1.00 Å from O(5) and with a valence angle of 105°, the contacts H...O(2) and H...O(4ⁱ) would be 2.1 (2) and 2.5 (2) Å respectively and angles H—O(5)...Naⁱ and H—O(5)...Naⁱⁱⁱ would be 114 (3) and 119 (3)° respectively, and the angle between the plane of the water atoms and that of O(5), Naⁱ, Naⁱⁱⁱ would be 86 (3)°. Alternately, the water could make a bifurcated hydrogen bond with the pair of twofold-symmetry-related oxygens O(2) and a simple hydrogen bond with O(4ⁱ). In fact, if the H atom is assumed to be 1.00 Å from the water O atom along the twofold axis on the side of O(2) and O(2ⁱⁱ) (see Fig. 4), the H...O(2) contact and the H—O(5)...O(4ⁱ) angle would be 2.2 (2) Å and 103 (3)° respectively. If one H atom is on the twofold axis, the other would be disordered, distributed in the two O(5)...O(4ⁱ) and O(5)...O(4ⁱⁱⁱ) directions with 0.5 occupancy. The angle between the plane of the water atoms and that of O(5), Naⁱ, Naⁱⁱⁱ would be 85 (3)°. Fig. 5 shows projections on the *ab* plane of the sodium ions and the sulfate groups which lie on the same side of a polar region: each polar head is surrounded by three water molecules and three counterions, and, at longer distances, by six polar heads in a hexagonal fashion. The strong ionic interactions together with the weak hydrogen bonds control the crystal packing.

Much weaker van der Waals interactions are present in the apolar region. Although the hydrocarbon chains are tilted with respect to the normal to the polar region (see Fig. 2), they do not give rise to short intermolecular contacts. This is also reflected by the atomic thermal factors which increase along the chain from the polar head to the terminal methyl group. Only one van der Waals contact of 3.80 (2) Å between two twofold-symmetry-related methyl C atoms occurs within the tail-to-tail region.

In the crystal packing found by Sundell (1977), the ratio of water: SDS (1:8), four times smaller than in our case, does not allow hydrogen-bond formation for each sulfate group. The polar head of only one of the four independent SDS chains participates in hydrogen bonding, the other sulfate groups being cemented only by the Na⁺ ions. In the double layer observed by Sundell (1977), the hydrocarbon chains are almost perpendicular to the polar-head-layer plane (79°), while in our case the chain is more tilted, the angle between the mean line passing through the hydrocarbon chain and the polar plane (*ab* plane) being 46.4 (9)°. This tilting causes a shrinking of the lamellar thickness, which decreases from 39.3 Å (corresponding to half the length of the *a* axis, since the unit cell contains two

double layers) in the case of Sundell to 30.8 Å (corresponding to the length of the *c* axis) in our case. The chain tilting and therefore the shrinking of the lamellar size seem to be related to the area per polar head in the layer plane which increases from 20.9 Å² in the case of Sundell to 25.8 Å² in our case ($a \times b/2$).

Table 3. Angles (°) occurring around the water molecule

| E.s.d.'s are in the range 0.2–0.3°. | | | |
|-------------------------------------|-------|--|-------|
| O(2)...O(5)...O(2 ⁱⁱ) | 64.4 | O(4 ⁱ)...O(5)...O(4 ⁱⁱⁱ) | 154.2 |
| O(2)...O(5)...O(4 ⁱⁱⁱ) | 135.1 | O(4 ⁱ)...O(5)...Na ⁱⁱⁱ | 84.3 |
| O(2)...O(5)...O(4 ⁱ) | 70.7 | Na ⁱ ...O(5)...Na ⁱⁱⁱ | 86.6 |

Symmetry code: (i) $x, y-1, z$; (ii) $-x+1, y, -z$; (iii) $-x+1, y-1, -z$.

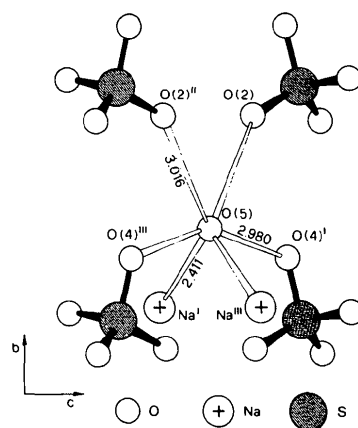


Fig. 4. The interactions of a water molecule with the surrounding atoms. E.s.d.'s are 0.009 and 0.006 Å for the contacts that O(5) forms with O(2) and O(4ⁱ) respectively and 0.006 Å for the O...Na contact. The symmetry code is the same as that in Table 3.

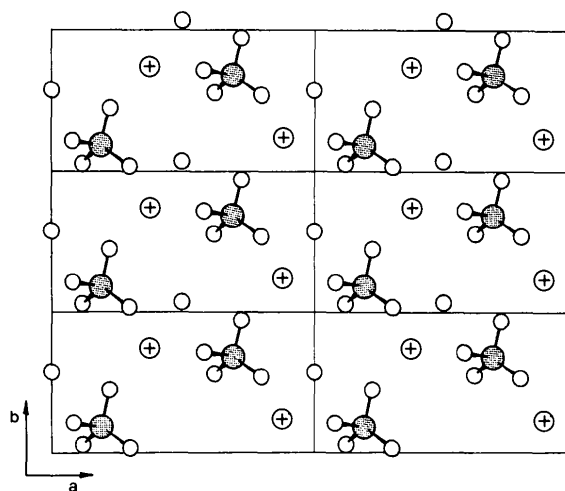


Fig. 5. A projection on the *ab* plane of the sulfate groups and Na⁺ ions which lie on the same side of a polar region. Isolated open circles represent water molecules.

A similar situation has been found in the study of the molecular packing of glycerolipids, where an extreme chain tilt of 60° has been observed in the crystal structure of 2,3-dilauroyl-D-glycerol (Pascher, Sundell & Hauser, 1981). These authors underline that in a bilayer structure the chain tilt increases with the space requirement of the head group according to the relation $\cos \varphi = \Sigma/S$ where φ , Σ and S stand for the chain tilt angle, the area of cross section of the hydrocarbon chain and the area per polar head in the layer plane respectively.

Crystals of a second triclinic phase of SDS have been obtained from aqueous solution and are under structural investigation. Simultaneously work is in progress in order to correlate the structural information obtained from crystal phases with that of micellar aggregates in aqueous solution.

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Oligophosphine Ligands. XVII.* *trans*-Bis(dinitrogen)-*mer*-[bis(3-diphenylphosphino-propyl)phenylphosphine](trimethylphosphine)molybdenum(0)

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Abstract. $[\text{Mo}(\text{N}_2)_2\{\text{P}(\text{CH}_3)_2\}\{\text{P}(\text{C}_6\text{H}_5)_1(\text{CH}_2)_3\text{P}(\text{C}_6\text{H}_5)_2\}_2]$, $M_r = 790.66$, orthorhombic, $P2_12_12_1$, $a = 10.893$ (2), $b = 15.573$ (3), $c = 22.989$ (5) Å, $V = 3900$ (1) Å³, $Z = 4$, $D_x = 1.347$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 4.66$ cm⁻¹, $F(000) = 1640$, $T = 293$ K, $R = 0.037$ for 4104 observed reflexions. The X-ray study has shown the presence of two dinitrogen ligands in *trans* positions, with the phosphines lying in the equatorial plane of the coordination octahedron. The Mo–N bond lengths are 1.998 (4) and 2.031 (4) Å, and the Mo–P distances within the six-membered chelate rings are 2.438 (1)–2.481 (1) Å. The Mo–P(CH₃)₃ separation is 2.508 (1) Å.

Introduction. The crystal structure of the title compound, synthesized as described in a previous paper (Dahlenburg & Pietsch, 1986), has been determined as part of a broad study of bis(dinitrogen)molybdenum

complexes containing flexible trimethylene-linked tris(tertiary phosphine) ligands.

Experimental. Orange, transparent crystals of the compound under investigation were grown from tetrahydrofuran/methanol at room temperature, and a fragment of approximate dimensions $0.2 \times 0.2 \times 0.3$ mm was used for all X-ray measurements. Syntex $P2_1$ diffractometer; graphite-monochromated Mo $K\alpha$ radiation; cell parameters by least-squares refinement of the setting angles of 15 reflexions within $16 < 2\theta < 25^\circ$; intensity measurements by $\theta/2\theta$ scans ($4.5 \leq 2\theta \leq 55^\circ$, $0 \leq h \leq 14$, $0 \leq k \leq 20$, $0 \leq l \leq 29$); no significant decline in intensity for three standards monitored every 100 reflexions. 5029 data (all unique) collected out of which 29 systematically absent ($h00$, $0k0$, $00l$ for h , k and l odd, respectively), 893 unobserved [$|F_o| < 4\sigma(F_o)$], and three suppressed (111, 022, and 041 which apparently suffered from secondary extinction). Lorentz–polarization correction, absorption ignored. Structure solved by Patterson and

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