bonds while as an acceptor in the third with the imino nitrogen N(11). There is one water molecule in the asymmetric unit which acts as a strong stabilizing force since the water O atom is coordinated to the Na atom and it also acts as a proton donor in the hydrogen bond with the carbonyl oxygen O(14) of the acetamido moiety and the imino nitrogen N(11) of the symmetry-related molecule. Though all the sulfacetamide molecules, water molecules and Na atoms are linked strongly through hydrogen bonds and coordinating bonds, the non-polar ring moieties are stacked in such a way that they also generate significant van der Waals interactions between them.

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Structure of Tetracarbonyl(5,7,12,14-tetramethyldibenzo[b, i][1,4,8,11]-tetraazacyclotetradeca-2,4,6,9,11,14-hexaene)molybdenum(0)

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Abstract. [Mo(CO)$_4$(C$_{22}$H$_{24}$N$_4$)], $M_r = 552.4$, triclinic, $P\bar{1}$, $a = 8.909$ (6), $b = 9.361$ (6), $c = 16.544$ (6) Å, $\alpha = 89.36$ (4), $\beta = 78.03$ (5), $\gamma = 67.77$ (5)°, $V = 1246$ Å^3, $Z = 2$, $D_x = 1.473$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.521$ mm^{-1}, $F(000) = 564$, $T = 298$ K, $R = 0.0502$ for 2958 observed reflections. Two of the four N atoms of the cyclic ligand are coordinated in a *cis* configuration to the Mo(CO)$_4$ fragment, giving a distorted octahedral environment at Mo with the macrocycle folded away from the metal centre.

Introduction. The tetradentate macrocyclic ligand 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraazacyclotetradeca-2,4,6,9,11,13-hexaene ($L = H_2L'$) exhibits a range of conformations when bound to metal

ions as the dianion (L'^{2-}). Compounds that have been prepared include square planar complexes with bivalent and trivalent metal centres (Jäger, 1964; Goedken, Pluth, Peng & Burnsten, 1976), five-coordinate square-based pyramidal species (Weiss, Burnsten, Peng & Goedken, 1976; Warren & Goedken, 1978) and octahedral complexes incorporating two mutually *cis* (Goedken & Ladd, 1982) and *trans* (Weiss & Goedken, 1976) ligands.

L' L
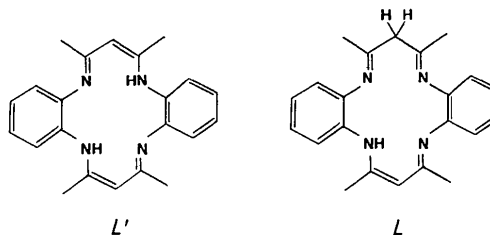
A monomeric complex formed by reaction of $Mo(CO)_6$ with H_2L' has been formulated as $Mo(CO)_4$-(H_2L) (Bell & Dabrowiak, 1975); IR spectra of this product indicate a *cis* coordination of H_2L to the $Mo(CO)_4$ moiety, while ^1H NMR spectra suggest that migration of one of the amino protons to the methine C atom of the diiminato ring has occurred, with the other amino proton retained. The determination of the single-crystal structure was undertaken with a view to investigating these structural predictions and assessing the conformation adopted by the macrocycle in the complex.

Experimental. Compound synthesized as described previously (Bell & Dabrowiak, 1975), crystals suitable for diffraction obtained by recrystallization from diglyme; yellow, tabular crystal, $0.02 \times 0.03 \times 0.04$ cm, space group identified by combination of oscillation and Weissenberg photography, E statistics and successful refinement. D_m not determined. CAD-4 diffractometer, 298 K, 16 reflections ($11.5 < \theta < 14.5°$) centred, graphite-monochromated Mo $K\alpha$ X-radiation.

For data collection $\theta_{max} = 22.5°$, ω–2θ scan in 96 steps, ω scan width $1.0 + 0.5°$ tanθ, rapid pre-scan after which reflections with $I > \sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to

maximum measuring time of 60 s, crystal orientation checked every 200 reflections, two intensity standards, no significant crystal movement or decay, 3241 unique data over 36 X-ray hours, $h -9\rightarrow9$, $k -10\rightarrow10$, $l \, 0\rightarrow17$, no absorption correction.

For structure solution and refinement 2958 amplitudes $[F > 6\sigma(F)]$, Patterson and successive Fourier difference syntheses (Sheldrick, 1976), full-matrix least-squares (F), $w^{-1} = [\sigma^2(F) + 0.00023F^2]$, anisotropic thermal parameters for Mo, O and N, isotropic for C; H atoms refined in fixed, calculated positions except for H(4N), $R = 0.0502$, $wR = 0.0706$, $S = 1.30$, data: variable ratio 16:1, $(\Delta/\sigma)_{max}$ in final cycle <0.04, max. peak and min. trough in final ΔF synthesis 0.77 and -1.05 e Å^{-3} respectively. No correction for secondary extinction. Neutral scattering factors for C, H, O, N (Sheldrick, 1976) and Mo (Cromer & Mann, 1968), computer programs *SHELX76* (Sheldrick, 1976), *CALC* (Gould & Taylor, 1983), *ORTEP*II (Mallinson & Muir, 1985).

Discussion. Table 1 lists fractional coordinates while those calculated for H atoms other than H(4N) have been deposited as Table 5; anisotropic thermal parameters have been deposited as Table 6.† Fig. 1 is a view along a direction approximately normal to the molecular least-squares plane while Fig. 2 clarifies the conformation of the ligand and its orientation with respect to the $Mo(CO)_4$ moiety. The single-crystal X-ray structure of $[Mo(CO)_4(H_2L)]$ shows a distorted octahedral stereochemistry around Mo with the macrocycle bound in a *cis* manner to the metal ion, Mo–N(1) = 2.271 (4), Mo–N(11) = 2.278 (4) Å, $\angle$N(1)MoN(11) = 78.76 (16)°. The Mo–C distances *trans* to N are significantly shorter [Mo–C(1*) = 1.956 (6), Mo–C(2*) = 1.957 (6) Å] than those *cis* to N [Mo–C(3*) = 2.027 (6), Mo–C(4*) = 2.008 (6) Å]. The macrocycle adopts a symmetrical conformation with an approximate mirror plane of symmetry passing through Mo(1), C(3*), O(3), C(4*), O(4), C(6) and C(13). Tables 2, 3 and 4 summarize bond lengths, angles and least-squares planes for the molecule respectively while torsion angles have been deposited as Table 7. The overall shape of the molecule is well illustrated by a series of least-squares mean planes and the angles formed by their normals (Table 4). The angle between the normals to planes 1 and 2 can also be expressed as the internal hinge angle of the planes, with a value of 115°. The benzo rings are upswept, approximately equally, from the plane of the four N atoms towards Mo(1).

Table 1. *Fractional coordinates of atoms with e.s.d.'s in parentheses*

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

	x	y	z	$U_{eq}(Å^2)$
Mo(1)	0.40479 (5)	0.20879 (4)	0.20881 (3)	0.0339 (4)
C(1*)	0.5636 (7)	0.2771 (7)	0.1358 (4)	0.0473 (15)
O(1)	0.6548 (5)	0.3196 (6)	0.0925 (3)	0.085 (4)
C(2*)	0.3013 (7)	0.4141 (7)	0.2680 (4)	0.0460 (14)
O(2)	0.2395 (7)	0.5356 (5)	0.3011 (4)	0.085 (4)
C(3*)	0.2641 (7)	0.3053 (7)	0.1257 (4)	0.0450 (14)
O(3)	0.1992 (6)	0.3734 (5)	0.0767 (3)	0.079 (4)
C(4*)	0.5688 (7)	0.1588 (7)	0.2821 (4)	0.0468 (14)
O(4)	0.6670 (7)	0.1478 (6)	0.3195 (3)	0.091 (4)
N(1)	0.5048 (5)	-0.0358 (5)	0.1489 (3)	0.034 (3)
N(4)	0.6845 (6)	-0.2370 (5)	0.2505 (3)	0.041 (3)
N(8)	0.4341 (5)	-0.1097 (5)	0.3789 (3)	0.043 (3)
N(11)	0.2370 (5)	0.1072 (5)	0.2909 (3)	0.035 (3)
C(2)	0.6826 (6)	-0.1117 (6)	0.1232 (3)	0.0338 (12)
C(3)	0.7718 (6)	-0.2128 (6)	0.1746 (3)	0.0350 (12)
C(5)	0.6961 (7)	-0.3748 (6)	0.2809 (4)	0.0423 (14)
C(5A)	0.8182 (8)	-0.5216 (7)	0.2346 (4)	0.0591 (17)
C(6)	0.5901 (7)	-0.3793 (7)	0.3533 (4)	0.0461 (14)
C(7)	0.4608 (7)	-0.2515 (7)	0.4010 (4)	0.0442 (14)
C(7A)	0.3530 (8)	-0.2860 (8)	0.4757 (4)	0.0643 (18)
C(9)	0.3098 (6)	0.0263 (6)	0.4229 (3)	0.0378 (12)
C(10)	0.2091 (6)	0.1362 (6)	0.3794 (3)	0.0336 (12)
C(12)	0.1829 (6)	0.0124 (6)	0.2642 (3)	0.0346 (12)
C(12A)	0.0819 (7)	-0.0636 (7)	0.3162 (4)	0.0486 (15)
C(13)	0.2276 (6)	-0.0280 (6)	0.1719 (3)	0.0387 (12)
C(14)	0.4134 (6)	-0.1109 (6)	0.1425 (3)	0.0360 (12)
C(14A)	0.4740 (7)	-0.2755 (7)	0.1097 (4)	0.0502 (15)
C(15)	0.7623 (7)	-0.0808 (6)	0.0489 (4)	0.0428 (14)
C(16)	0.9332 (7)	-0.1528 (7)	0.0230 (4)	0.0497 (15)
C(17)	1.0233 (7)	-0.2520 (7)	0.0724 (4)	0.0497 (15)
C(18)	0.9436 (7)	-0.2791 (7)	0.1486 (4)	0.0444 (14)
C(19)	0.2898 (7)	0.0597 (7)	0.5073 (4)	0.0485 (14)
C(20)	0.1684 (7)	0.1971 (7)	0.5461 (4)	0.0533 (16)
C(21)	0.0665 (8)	0.3003 (7)	0.5035 (4)	0.0552 (16)
C(22)	0.0882 (7)	0.2717 (7)	0.4196 (4)	0.0475 (14)
H(4N)	0.609 (7)	-0.158 (7)	0.275 (4)	0.0500

† Lists of structure factors, Tables 5–7 and fuller versions of Tables 2 and 3 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43609 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The crystal structure of the complex confirms protonation of the methine C(13) atom with C(12)—N(11) = 1·278 (7), C(14)—N(1) = 1·281 (7) Å indicating C—N double-bond character for these linkages. The amine hydrogen is on N(4) with a secondary contact to N(8), while bond lengths of 1·374 (9) and 1·408 (9) Å for C(5)—C(6) and C(6)—C(7), and 1·351 (8) and 1·318 (8) Å for N(4)—C(5) and N(8)—C(7) respectively are consistent with the canonical form (A) for the N(4)→N(8) chain.

Very recently the related complex [Mo(CO)$_4$$L_1$] ($L_1$ = 6,7,16,17-tetrahydro-15H-dibenzo[e,n][1,4,8,12]-dioxadiazacyclopentadecine – incorporating a potential O$_2$N$_2$ donor set) has been prepared (Leoni, Grilli, Pasquali & Tomassini, 1985) in which the Mo(CO)$_4$ moiety is bound likewise to two N-donor atoms of the macrocycle in a *cis* manner.
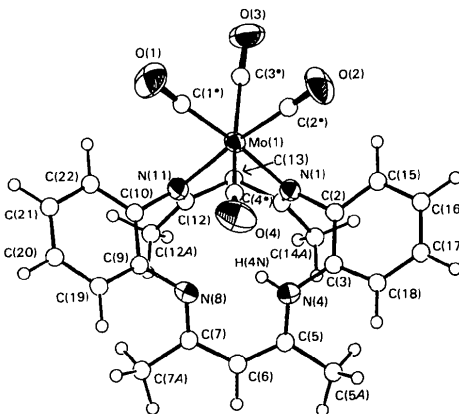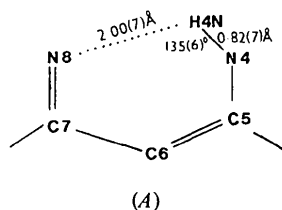
(A)

Fig. 1. *ORTEP* view of the molecule, with thermal ellipsoids drawn at the 50% electron probability level, excepting C and H which have artificial radii of 0·15 and 0·10 Å respectively for clarity.
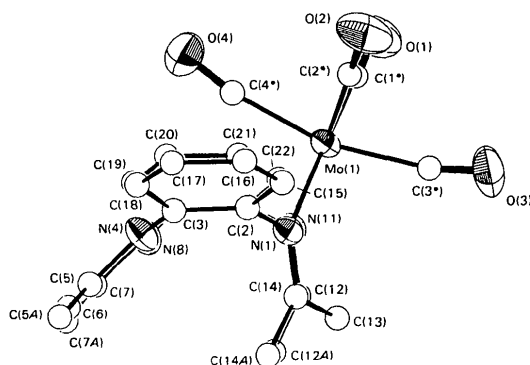

Fig. 2. View of the molecule along a direction normal to that in Fig. 1 to illustrate the macrocycle conformation. C(9) and C(10) are wholly obscured by C(3) and C(2) respectively. H atoms are omitted and C atoms have artificial radius of 0·15 Å for clarity.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

Mo(1)—C(1*)	1·956 (6)	N(11)—C(12)	1·278 (7)
Mo(1)—C(2*)	1·957 (6)	C(2)—C(3)	1·394 (8)
Mo(1)—C(3*)	2·027 (6)	C(2)—C(15)	1·372 (8)
Mo(1)—C(4*)	2·008 (6)	C(3)—C(18)	1·388 (8)
Mo(1)—N(1)	2·271 (4)	C(5)—C(5A)	1·485 (9)
Mo(1)—N(11)	2·278 (4)	C(5)—C(6)	1·374 (9)
N(1)—C(2)	1·439 (7)	C(6)—C(7)	1·408 (9)
N(1)—C(14)	1·281 (7)	C(7)—C(7A)	1·511 (10)
N(4)—H(4N)	0·82 (7)	C(9)—C(10)	1·391 (8)
N(4)—C(3)	1·398 (7)	C(12)—C(12A)	1·484 (8)
N(4)—C(5)	1·354 (8)	C(12)—C(13)	1·510 (8)
N(8)—C(7)	1·318 (8)	C(13)—C(14)	1·510 (8)
N(8)—C(9)	1·412 (7)	C(14)—C(14A)	1·492 (8)
N(11)—C(10)	1·444 (7)		

Table 3. *Angles* (°) *with e.s.d.'s in parentheses*

C(1*)—Mo(1)—C(2*)	89·3 (3)	Mo(1)—N(11)—C(10)	117·1 (3)
C(1*)—Mo(1)—C(3*)	82·3 (3)	Mo(1)—N(11)—C(12)	124·1 (4)
C(1*)—Mo(1)—C(4*)	84·0 (3)	C(10)—N(11)—C(12)	118·2 (5)
C(1*)—Mo(1)—N(1)	96·54 (22)	N(1)—C(2)—C(3)	119·7 (5)
C(1*)—Mo(1)—N(11)	174·87 (22)	N(1)—C(2)—C(15)	119·3 (5)
C(2*)—Mo(1)—C(3*)	85·5 (3)	N(4)—C(3)—C(2)	118·5 (5)
C(2*)—Mo(1)—C(4*)	86·3 (3)	N(4)—C(3)—C(18)	123·8 (5)
C(2*)—Mo(1)—N(1)	174·16 (22)	N(4)—C(5)—C(5A)	120·3 (5)
C(2*)—Mo(1)—N(11)	95·41 (22)	N(4)—C(5)—C(6)	119·9 (5)
C(3*)—Mo(1)—C(4*)	164·1 (3)	N(8)—C(7)—C(6)	120·5 (5)
C(3*)—Mo(1)—N(1)	95·05 (21)	N(8)—C(7)—C(7A)	122·6 (6)
C(3*)—Mo(1)—N(11)	100·10 (21)	C(6)—C(7)—C(7A)	116·9 (6)
C(4*)—Mo(1)—N(1)	94·44 (21)	N(8)—C(9)—C(10)	118·8 (5)
C(4*)—Mo(1)—N(11)	94·25 (21)	N(8)—C(9)—C(19)	122·9 (5)
N(1)—Mo(1)—N(11)	78·76 (16)	N(11)—C(10)—C(9)	118·6 (5)
Mo(1)—N(1)—C(2)	116·6 (3)	N(11)—C(10)—C(22)	120·8 (5)
Mo(1)—N(1)—C(14)	123·8 (4)	N(11)—C(12)—C(12A)	125·7 (5)
C(2)—N(1)—C(14)	119·4 (5)	N(11)—C(12)—C(13)	117·3 (5)
H(4N)—N(4)—C(3)	114 (5)	N(1)—C(14)—C(13)	117·8 (5)
H(4N)—N(4)—C(5)	118 (5)	N(1)—C(14)—C(14A)	125·8 (5)
C(3)—N(4)—C(5)	127·1 (5)	C(13)—C(14)—C(14A)	116·4 (5)
C(7)—N(8)—C(9)	125·1 (5)		

Table 4. *Selected least-squares mean planes and interplanar angles*

Plane	Atoms in plane	R.m.s. deviation of atoms from plane (Å)
1	Mo(1)C(1*)O(1)C(2*)O(2)N(1)N(11)	0·059
2	N(1)N(4)N(8)N(11)	0·037
3	N(4)C(5)C(6)C(7)N(8)	0·013
4	C(2)C(3)C(15)C(16)C(17)C(18)	0·029
5	C(9)C(10)C(19)C(20)C(21)C(22)	0·031
6	Mo(1)C(3*)O(3)C(4*)O(4)C(6)C(13)	0·240

Interplanar angles (°) with e.s.d.'s in parentheses

1–2	65·00 (12)	2–4	21·57 (16)	1–6	89·74 (7)
1–3	23·53 (22)	2–5	24·54 (19)	2–6	89·83 (11)
1–4	67·45 (14)	3–4	46·33 (24)	3–6	89·64 (14)
1–5	70·49 (16)	3–5	49·91 (22)	4–6	68·28 (15)
2–3	41·48 (22)	4–5	45·95 (20)	5–6	65·85 (17)

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Structure of a Triclinic Phase of Sodium Dodecyl Sulfate Monohydrate. A Comparison with Other Sodium Dodecyl Sulfate Crystal Phases

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Abstract. $Na^+.C_{12}H_{25}O_4S^-.H_2O$, $M_r = 306.4$, triclinic, $P\bar{1}$, $a = 10.423$ (4), $b = 5.662$ (3), $c = 28.913$ (12) Å, $\alpha = 86.70$ (4), $\beta = 93.44$ (4), $\gamma = 89.55$ (4)°, $V = 1700$ (1) Å³, $Z = 4$, $D_x = 1.20$ g cm⁻³, $\lambda(Cu\ K\alpha) = 1.5418$ Å, $\mu = 20$ cm⁻¹, $F(000) = 664$, $T = 290$–294 K, $R = 0.11$ for 4457 observed reflections. Each asymmetric unit is made up of two water and two sodium dodecyl sulfate (SDS) molecules with different conformations. The SDS molecules form a lamellar structure with regions alternately polar and apolar. Adjacent polar heads of the same monolayer are displaced in a zigzag fashion along the *a* axis forming a rippled structure. Facing monolayers are held together by Coulombic interactions not screened by the water molecules. Weak van der Waals interactions are present in the apolar region. From comparison of the present phase with other SDS crystal phases differing in water content it is possible to deduce that the higher the water content, the larger the average area per polar head and the smaller the lamellar thickness. In all the crystal phases interdigitation of hydrocarbon chains does not take place, whereas the polar heads can give rise to planar or rippled monolayers.

Introduction. The alkali-metal dodecyl sulfates form micellar aggregates in aqueous solutions; in particular sodium dodecyl sulfate forms micelles 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 the polar head and the non-polar hydrocarbon chain ending with a methyl group. Among the micellar systems that of SDS is one of the most studied because of its wide variety of applications as a detergent. The knowledge of the aggregation mode of SDS molecules in micelles is necessary to understand the SDS behaviour in aqueous solution and the role at the molecular level of micelles in fields such as detergency, separation science, micellar catalysis and so on. In fact 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).

We think that the aggregation model of a surfactant observed in the solid state may be present in micellar solutions (Conte, Di Blasi, Giglio, Parretta & Pavel, 1984). For this purpose we have undertaken the structural determination of those SDS crystal phases that can be obtained from aqueous solutions at different concentrations and temperatures in order to check the corresponding structural units in the study of the micellar solutions.

Experimental. SDS was purchased from Sigma Chemical Co. Single crystals in the form of colourless prisms were obtained by dissolving SDS in water (32 wt%) within a temperature range 290–294 K. A crystal of 1 × 0.5 × 0.05 mm was mounted on an automatic Syntex $P2_1$ diffractometer equipped with a graphite monochromator and Cu $K\alpha$ radiation. The unit-cell parameters were determined from a least-

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