la chaîne S—C—C—S du dithiolate, ce qui est en faveur de la structure (*c*) et corrobore les autres études physicochimiques. La légère disymétrie du dithiolato—Ni peut être attribuée au branchement du cycle benzyle.

Le noyau central est parfaitement plan; le cycle phényle fait un angle de 7,5 (5)° avec ce dernier. La chaîne aliphatique est pratiquement étendue, son plan moyen faisant un angle de 63° avec le cycle phényle, ce qui confère à la molécule une forme en zigzag (Fig. 2).

Les molécules ont leur axe longitudinal situé dans des plans sensiblement parallèles au plan (302). Si l'on définit l'axe moléculaire par l'atome 12 et son homologue 12′, l'angle formé par cet axe et le plan ($x0z$) est proche de 18°. Chaque ensemble constitué des molécules qui se déduisent les unes des autres par l'intermédiaire de centres de symétrie forme un feuillet parallèle à Oy, pratiquement parallèle au plan (202). Les molécules d'un même feuillet sont en interaction par l'intermédiaire de leurs chaînes aliphatiques antiparallèles (Fig. 2). Bien que ces interactions résultent des forces de van der Waals, l'énergie d'interaction intermoléculaire, responsable de la cohésion cristalline, est certainement appréciable, par suite du nombre important d'atomes en contact.

Soulignons l'interpénétration des chaînes alkyles pouvant conduire à une couche de type smectique d'épaisseur nettement inférieure à la longueur des molécules. Les noyaux dithiolate de nickel sont situés dans des plans parallèles séparés par une distance de 3,57 Å mais ne sont pas superposés.

L'arrangement moléculaire est très proche de celui de l'acide *n*-heptyloxybenzoïque (Bryan & Miller, 1980) et présente quelques points communs avec celui du bromo-17 heptadécanoate de cholestérol (Abrahamsson & Dahlén, 1976) qui possèdent tous deux une phase smectique *C*.

Dans la plupart des structures cristallines connues de composés mésogènes, la molécule est approximativement linéaire ('rod-like'). La molécule présentement étudiée adopte dans le cristal, une conformation en zigzag, identique à celles du dimère de l'acide *n*-heptyloxybenzoïque, du bis[(*n*-butyl)-4 phényl-2,6 tétrathiafulvalène (Polycarpe, 1982) et du bromo-17 heptadécanoate de cholestérol. Par contre, le diheptyloxy-4,4′ azoxybenzène, smectique *C*, s'il adopte une forme allongée dans le cristal (Cotrait, Marsau & Pesquer, 1979), montre dans la mésophase (étude RPE par la méthode des sondes de spin) une conformation de type zigzag (Sanson & Ptak, 1981). On peut donc penser qu'un telle conformation est caractéristique des smectogènes de type *C*. D'autres études devront confirmer cette hypothèse.

Nous remercions vivement M Giral et Mme Toreilles pour les conseils et l'aide qu'ils nous ont prodiguées dans la synthèse du produit étudié.

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Structure of Bis(tetraethylammonium) Tetrathiomolybdate(VI), $2C_8H_{20}N^+.MoS_4{}^{2-}$

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Abstract. $M_r = 484{\cdot}7$, triclinic, $P\bar{1}$, $a = 13{\cdot}079\ (2)$, $b = 13{\cdot}617\ (2)$, $c = 16{\cdot}111\ (2)$ Å, $\alpha = 111{\cdot}30\ (1)$, $\beta = 112{\cdot}44\ (1)$, $\gamma = 90{\cdot}92\ (1)°$, $V = 2430{\cdot}62\ (58)$ Å^3, $Z = 2$, $D_m = 1{\cdot}33$, $D_x = 1{\cdot}32$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å, $\mu = 8{\cdot}6$ cm^{-1}, $F(000) = 512$, $T = 293$ K, $R = 3{\cdot}4$, $R_w = 4{\cdot}8\%$ for 4863 unique reflections having

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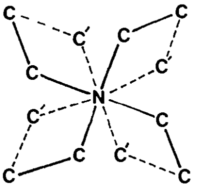
$F_o^2 > 3\sigma(F_o^2)$. There are two crystallographically independent MoS_4^{2-} anions per asymmetric unit with no imposed symmetry. The Mo—S distance ranges from 2·167 (1) to 2·187 (2) Å with a mean of 2·177 (6) Å and a nearly perfect tetrahedral S—Mo—S angle of 109·47 (87)°.

Introduction. Evidence for possible involvement of the MoS_4^{2-} anion as a structural component in the nitrogenase active site has been reported (Zumft, 1978). This result stimulated us to investigate the synthesis of high Fe—Mo—S polynuclear aggregates, utilizing the MoS_4^{2-} as ligand for transition-metal ions in various complexes. The MoS_4^{2-}–$Fe(L)_n$ ligand exchange reactions used in our laboratories for the synthesis of such species have been reviewed (Coucouvanis, 1981). The Mo—S distance in the MoS_4^{2-} unit undergoes considerable changes which might reflect $M \rightarrow Mo$ charge transfer. To assess any significance of these changes, the Mo—S distance in the undistributed free MoS_4^{2-} unit in a similar lattice environment must be accurately known.

Experimental. $[Et_4N]_2MoS_4$ (Coucouvanis, 1981) grown by slow diffusion of ether in an acetonitrile solution of the sample, determination of cell dimensions and collection of intensity data carried out with a computer-controlled Nicolet XRD P3 diffractometer equipped with a graphite crystal monochromator, lattice constants determined from least-squares refinement of $2\theta,\omega,\varphi,\chi$ diffractometer angles of 24 centered independent reflections, $25 < 2\theta < 45°$, D_m by flotation using CCl_4/pentane; intensity data were collected at room temperature, θ–2θ scan mode, variable scan speed 6·0–29·3° s^{-1}, full-sphere data, $2\theta_{max} = 45°$, crystal 0·30 × 0·25 × 0·32 mm; three standard reflections measured every 60 reflections showed no fluctuations greater than ±5%, 6372 reflections measured, 4863 with $F_o^2 > 3\sigma(F_o^2)$ were used in least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 0{\cdot}0$ if $F_o^2 < 3\sigma(F_o^2)$, $w = 1/\sigma^2(F_o^2)$ for all others, 407 variables, no absorption correction.

The crystal system, cell parameters and density information suggested two crystallographically independent MoS_4^{2-} anions. Positions of the two Mo atoms obtained by direct methods (*MULTAN*; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), confirmed by three-dimensional Patterson synthesis; S and cation atoms located on subsequent Fourier syntheses following full-matrix least-squares refinement of the input atomic coordinates; after six cycles of refinement $R = 9{\cdot}2$, $R_w = 14{\cdot}11\%$. Temperature factors of the methylenic carbons of one of the tetraethylammonium cations were abnormally high and disorder was suspected. A difference Fourier map calculated giving 50% occupancy to those carbons revealed the positions of four other carbons in tetrahedral orientation around the N(3) atom. After four more cycles of refinement $R_w = 6{\cdot}89$ and $R = 4{\cdot}7\%$. At this point four more low-weight peaks corresponding to methylenic carbons around the N(4) and four around the N(2) at an approximate N—C distance of 1·5 Å were revealed. To those carbon atoms 25 and 15% occupancy was given respectively. The carbon atoms of the second cation with 15% occupancy were not refined. After two more cycles of refinement $R_w = 6{\cdot}10$ and $R = 4{\cdot}15\%$; idealized H-atom positions then included at 0·95 Å from C atoms with an overall temperature factor of 8·00 Å^2, H atoms attached to C atoms that were refined isotropically were given temperature factors equal to those of their corresponding C atoms. Further refinement including the H atoms in structure-factor calculation, but not refining them, converged to $R = 3{\cdot}4$; $R_w = 4{\cdot}8\%$.* Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The structure consists of loosely packed discrete MoS_4^{2-} anions and $(C_2H_5)_4N^+$ cations having no crystallographically imposed symmetry. During the structure solution and refinement positional disorder among the methylenic $-CH_2-$ groups of three of the four tetraethylammonium cations was revealed in varying degrees from cation to cation with the cation of N(3) having the maximum of 50% and that of N(2) the minimum of 15%. A schematic drawing of this kind of disorder is shown below.



The tetraethylammonium containing nitrogen atom N(1) does not show any trace of such disorder. Positional disorder of the methylenic carbon atoms in the tetraethylammonium cation has been previously observed in a number of cases (see, for example, Stucky, Folkers & Kistenmacher, 1967; Handy, Ruff & Dahl, 1970; Ruff, White & Dahl, 1971).

The average N—C distance for all the cations is 1·574 (12) Å and the mean C—C distance 1·467 (13) Å. There are no intermolecular contacts between anions and cations other than those of van der Waals type.

A stereoview of the packing diagram of $(Et_4N)_2MoS_4$ is displayed in Fig. 1. Positional and thermal parameters of all non-hydrogen atoms are shown in Table 1.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38444 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

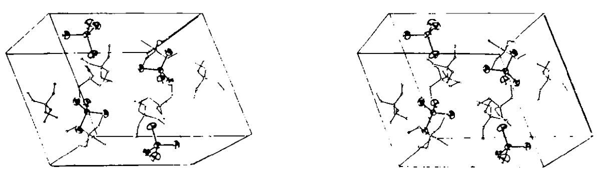

Fig. 1. *ORTEP* (Johnson, 1965) stereoview of the unit cell of $(Et_4N)_2MoS_4$.

Table 1. *Positional and thermal parameters and their e.s.d.'s in* $(Et_4N)_2MoS_4$

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} or B_{iso} (Å^2)
Mo(1)	0·36867 (3)	0·63688 (3)	0·74754 (3)	3·28 (2)
Mo(2)	0·90533 (4)	0·14896 (3)	0·77237 (3)	3·70 (2)
S(1)	0·4999 (1)	0·5832 (1)	0·8444 (1)	5·64 (7)
S(2)	0·2189 (1)	0·5122 (1)	0·6601 (1)	5·32 (7)
S(3)	0·3276 (1)	0·7810 (1)	0·8336 (1)	6·02 (8)
S(4)	0·4285 (1)	0·6723 (1)	0·6504 (1)	5·03 (7)
S(5)	0·9385 (1)	0·1622 (1)	0·9199 (1)	6·29 (8)
S(6)	0·8587 (1)	0·2991 (1)	0·7626 (1)	6·95 (9)
S(7)	0·7720 (2)	0·0131 (2)	0·6656 (2)	7·60 (10)
S(8)	1·0579 (1)	0·1260 (1)	0·7485 (1)	6·28 (10)
N(1)	0·5103 (3)	0·2970 (3)	0·5872 (3)	3·8 (2)
C(11)*	0·4794 (5)	0·1964 (4)	0·4974 (4)	5·3 (3)
C(12)	0·4117 (4)	0·3549 (4)	0·5762 (4)	5·7 (3)
C(13)	0·6131 (4)	0·3653 (4)	0·5991 (4)	4·6 (3)
C(14)	0·5425 (5)	0·2769 (5)	0·6797 (4)	6·5 (3)
C(15)	0·5667 (6)	0·1250 (5)	0·4981 (6)	7·8 (3)
C(16)	0·3685 (5)	0·3817 (5)	0·4870 (4)	6·5 (3)
C(17)	0·6512 (5)	0·4744 (4)	0·6796 (4)	5·4 (3)
C(18)	0·4551 (6)	0·1997 (6)	0·6770 (5)	8·0 (4)
N(2)	0·7945 (3)	0·4897 (3)	0·0572 (3)	3·8 (2)
C(21)	0·7682 (6)	0·5018 (6)	−0·0320 (5)	5·8 (4)
C(22)	0·6976 (5)	0·3985 (5)	0·0373 (5)	5·9 (3)
C(23)	0·8116 (6)	0·5772 (5)	0·1472 (5)	5·9 (3)
C(24)	0·9057 (6)	0·4370 (5)	0·0774 (5)	5·8 (3)
C(25)	0·8416 (6)	0·5975 (5)	−0·0191 (5)	7·2 (4)
C(26)	0·6800 (6)	0·2911 (5)	−0·0456 (5)	7·0 (4)
C(27)	0·9436 (6)	0·3993 (6)	0·1579 (5)	7·7 (4)
C(28)	0·7059 (6)	0·6285 (5)	0·1388 (6)	7·8 (4)
C′(21)†	0·875	0·563	0·063	5·000
C′(22)	0·672	0·532	0·055	5·000
C′(23)	0·864	0·454	0·149	5·000
C′(24)	0·750	0·375	0·047	5·000
N(3)	−0·0513 (4)	0·2182 (3)	0·4590 (3)	4·3 (2)
C(31)	0·022 (2)	0·137 (2)	0·476 (1)	10·1 (5)
C(32)	0·050 (1)	9·234 (1)	0·5479 (9)	6·1 (3)
C(33)	−0·108 (1)	0·312 (1)	0·470 (1)	7·0 (3)
C(34)	−0·157 (2)	0·169 (2)	0·379 (2)	12·3 (6)
C(35)	−0·2365 (7)	0·0830 (7)	0·3649 (7)	10·3 (5)
C(36)	0·1304 (7)	0·1594 (8)	0·5414 (7)	10·0 (6)
C(37)	0·404 (9)	0·2632 (9)	0·3605 (7)	12·6 (8)
C(38)	−0·1174 (7)	0·3744 (7)	0·5568 (6)	9·9 (5)
C′(31)	−0·133 (1)	0·121 (1)	0·445 (1)	7·6 (3)
C′(32)	−0·049 (1)	0·291 (1)	0·561 (1)	8·1 (3)
C′(33)	−0·034 (1)	0·183 (1)	0·365 (1)	7·7 (3)
C′(34)	0·009 (1)	0·301 (1)	0·436 (1)	6·7 (3)
N(4)	0·2773 (3)	0·0757 (3)	0·0606 (3)	3·7 (2)
C(41)	0·2280 (6)	−0·0408 (5)	−0·0069 (5)	5·3 (1)
C(42)	0·3928 (7)	0·0830 (6)	0·1322 (6)	6·5 (2)
C(43)	0·2789 (7)	0·1421 (6)	0·0049 (6)	6·3 (2)
C(44)	0·1982 (6)	0·1161 (6)	0·1122 (5)	5·9 (2)
C(45)	0·1189 (5)	−0·0615 (4)	−0·0932 (4)	5·1 (3)
C(46)	0·4100 (6)	0·0261 (6)	0·1966 (5)	7·8 (4)
C(47)	0·3465 (6)	0·1162 (6)	−0·0537 (5)	7·7 (4)
C(48)	0·2355 (6)	0·2235 (5)	0·1894 (5)	7·1 (4)
C′(41)	0·309 (2)	0·193 (2)	0·134 (1)	2·9 (4)
C′(42)	0·163 (2)	0·050 (1)	−0·013 (1)	2·3 (3)
C′(43)	0·366 (2)	0·070 (2)	0·014 (2)	3·3 (4)
C′(44)	0·306 (2)	−0·003 (2)	0·108 (1)	2·8 (4)

* The first number in the carbon-atom designation denotes the cation number.

† The prime designation is for the disordered carbon atoms.

Table 2. *Bond distances* (Å) *and angles* (°) *for the two* MoS_4 *anions*

In all cases the standard deviations from the mean have been obtained as follows: $\sigma = [\sum_{i=1}^{n}(x_i-\bar{x})^2/(N-1)]^{1/2}$, where x_i is the length of the bond and $\bar{x}$ is the mean value for the n equivalent bond lengths.

Mo–S		S–Mo–S	
Mo(1)–S(1)	2·175 (1)	S(1)–Mo(1)–S(2)	109·84 (8)
Mo(1)–S(2)	2·179 (1)	S(1)–Mo(1)–S(3)	109·75 (8)
Mo(1)–S(3)	2·167 (1)	S(1)–Mo(1)–S(4)	109·48 (8)
Mo(1)–S(4)	2·179 (1)	S(2)–Mo(1)–S(3)	109·60 (8)
Mean	2·175 (5)	S(2)–Mo(1)–S(4)	109·37 (8)
		S(3)–Mo(1)–S(4)	108·79 (7)
Mo(2)–S(5)	2·180 (2)	Mean	109·47 (37)
Mo(2)–S(6)	2·187 (2)		
Mo(2)–S(7)	2·171 (2)	S(5)–Mo(2)–S(6)	107·75 (8)
Mo(2)–S(8)	2·177 (2)	S(5)–Mo(2)–S(7)	109·51 (9)
Mean	2·179 (6)	S(5)–Mo(2)–S(8)	109·13 (8)
		S(6)–Mo(2)–S(7)	111·61 (9)
Overall mean	2·177 (6)	S(6)–Mo(2)–S(8)	109·26 (9)
		S(7)–Mo(2)–S(8)	109·53 (11)
		Mean	109·47 (1·24)
		Overall mean	109·47 (87)

The Mo(1)—S distances in the first anion range from 2·179 (1) to 2·167 (1) Å with an average of 2·175 (5) Å. The immediate coordination environment around the Mo(1) atom is nearly perfect tetrahedral with minimum and maximum S—Mo(1)—S angles of 108·79 (7) and 109·84 (8)° and an average of 109·47 (37)°, which is virtually identical to the theoretical value 109·5°. The S—S distances average 3·552 (9) Å.

The geometric parameters in the second anion are slightly different. It appears that this anion is slightly distorted from the tetrahedral configuration with Mo(2)—S distances ranging from 2·171 (2) to 2·187 (2) Å and S—Mo(2)—S angles from 107·75 (8) to 111·61 (9)° with an average of 109·47 (1·24)°. The mean Mo(2)—S and S—S distances are 2·179 (6) and 3·557 (4) Å, respectively, with an overall mean Mo—S distance of 2·177 (6) Å. The reason for the small (though insignificant) differences between the two anions is not apparent. However, the mean Mo—S and S—S distances are essentially equal within three standard deviations.

Detailed structural parameters of the two MoS_4^{2-} ions are shown in Table 2. The Mo—S distance in $(Et_4N)_2MoS_4$ compares with that in Cs_2MoOS_3, 2·179 (5) Å (Krebs, Müller & Kindler, 1970) and is in agreement with the Mo—S distance in the structure of $(NH_4)_2MoS_4$, 2·178 (6) Å (Lapasset, Chezeau & Belougne, 1976).

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Structure of Disodium Nitronitrosylbis[2,4,5,6(1*H*,3*H*)-pyrimidinetetrone 5-oximato(2−)]ruthenate(II) Heptahydrate, $Na_2[Ru(C_4HN_3O_4)_2(NO)(NO_2)].7H_2O$

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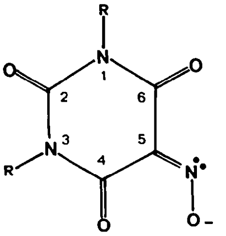
Abstract. $M_r = 659\cdot3$, $P\bar{1}$, $a = 17\cdot49$ (1), $b = 9\cdot44$ (1), $c = 6\cdot74$ (1) Å, $\alpha = 98\cdot67$ (5), $\beta = 96\cdot02$ (5), $\gamma = 90\cdot57$ (5)°, $U = 1094$ (1) Å^3, $Z = 2$, $D_x = 2\cdot00$, $D_m = 1\cdot96$ (5) Mg m^{-3} (by flotation), Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot86$ mm^{-1}, $F(000) = 660$, room temperature. Full-matrix refinement, 5979 reflections, gave $R = 0\cdot033$. The structure consists of Na^+ ions, water molecules and $[Ru(C_4HN_3O_4)_2(NO)(NO_2)]^{2-}$ dianions. The coordination about Ru is octahedral with NO and NO_2 ligands in *cis* arrangement. The Ru—N—O angle is 169·8 (2)°. The chelation of the ketone oximato ligand occurs *via* the atom of the oximato function and the 6-carbonyl function. The mechanism of the nitrosylation reaction is discussed in relationship to the structure of nitrosyl complexes.

Introduction. Ketone oximato ligands are known to stabilize Ru complexes (Brémard, Muller, Nowogrocki & Sueur, 1977). These nitrosyl complexes undergo nucleophilic attack at the nitrosyl group (Brémard, Nowogrocki & Sueur, 1979), as for metal–nitrosyl complexes with a sufficiently high degree of NO^+-like ligand character (Schüg & Guengerich, 1979; Walsh, Bullock & Meyer, 1980; Bottomley, 1978*a*). No X-ray structure of a ketone oximato nitrosyl complex has been reported. In view of the asymmetry of the ketone oximato ligands H_2vi^- and $dmvi^-$ several isomers are possible (Brémard *et al.*, 1977).



$R = H \rightarrow H_2vi^-$: monoanion of 2,4,5,6 (1*H*,3*H*)-pyrimidinetetrone 5-oxime.
$R = CH_3 \rightarrow dmvi^-$: the 1,3-dimethyl derivative.

Knowledge of the unequivocal structure is useful, in particular, for determining the mechanisms of (1), the reversible nitrosylation of $[Ru(H_2vi)_3]^-$ (Brémard *et al.*, 1979) and (2) the nitrosation of organic carbonyls containing an α-methylene group by $Ru(H_2vi)_2(NO)X$ and $Ru(dmvi)_2(NO)X$ (Brémard *et al.*, 1979) (X = Cl, Br, OH). The two series of nitrosyl complexes exhibit two different behaviors towards OH^-: $Ru(dmvi)_2(NO)X$ undergoes the expected nucleophilic attack while $Ru(H_2vi)_2(NO)X$ undergoes deprotonation of the H_2vi^- ligands (Sueur, Brémard & Nowogrocki, 1976). Herein we report the structure determination of $Na_2[Ru(Hvi)_2(NO)(NO_2)].7H_2O$.

Experimental. Solid $Ru(H_2vi)_3NO$, prepared as outlined previously (Brémard *et al.*, 1977), suspended in water (50 ml) was dissolved in NaOH (2×10^{-3}mol) added portionwise to the stirred suspension. A large excess of $NaNO_2$ (5×10^{-2}mol, 3·45 g) was dissolved in the

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