

The Crystal Structure of Tetramethylammonium Tris(*O*-cyclohexyl dithiocarbonato)nickelate(II) Acetone Solvate

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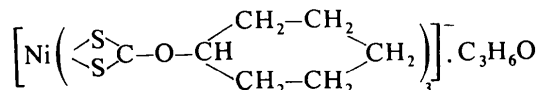
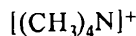
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Abstract

The crystal structure of the title compound, $C_{25}H_{45}NNiO_3S_6 \cdot C_3H_6O$, has been determined from three-dimensional intensities, measured on a computer-controlled Philips PW 1100 single-crystal diffractometer (1581 reflexions used). The crystals are monoclinic with $a = 12.593$ (6), $b = 17.776$ (8), $c = 16.589$ (6) Å, $\beta = 92.54$ (4)°, $Z = 4$ and space group Cc . The structure was solved by direct phase determination with *MULTAN*. The positional and thermal parameters of the atoms were refined by full-matrix least-squares calculations to a final $R = 0.060$ ($R_w = 0.051$). The anion shows approximate trigonal symmetry, with the Ni atom surrounded by six S atoms at the apices of a distorted octahedron. The Ni–S distances are in the range 2.393–2.469 Å, whereas in the dithiocarbonate ligands the C–S distances range between 1.65 and 1.69 Å and the C–O distances between 1.33 and 1.36 Å. The roughly planar anions form layers approximately parallel to (010) and are interconnected by the tetramethylammonium cations and the acetone molecules, which are distributed both within the layers and also between them.

Introduction

The crystal structure of tetramethylammonium tris(*O*-cyclohexyl dithiocarbonato)nickelate(II) acetone solvate (hereafter TMACXN)



was determined within the framework of a detailed structure investigation of the new ionic tris(dithiocarbonato) complexes of bivalent metals, recently prepared at the Inorganic Chemistry Laboratory of the University of Thessaloniki (Hatzikostas & Manoussakis, 1977). The structure of the first member of the series,

tetramethylammonium tris(*O*-isobutyl dithiocarbonato)nickelate(II) has been determined (Christidis & Rentzeperis, 1978).

Experimental

Good crystals of TMACXN were kindly provided by Professor G. Manoussakis and Mr C. Hatzikostas of the Inorganic Chemistry Laboratory. The selected crystal, a green prism with dimensions $0.3 \times 0.15 \times 0.11$ mm, was centred on our automatic Philips PW 1100 four-circle single-crystal diffractometer. Accurate cell parameters were obtained from direct measurement on the diffractometer of the θ angles of 135 reflexions with large θ values. The measurements were processed with the least-squares program *PARAM* [part of the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)]. The final values obtained are listed in Table 1. The density of the crystal was measured with a pycnometer.

From systematic absences the two space groups $C2/c$ and Cc came into consideration. Since only four formula units are contained in the unit cell and no centre of symmetry is expected for the dithiocarbonate anion, the space group Cc seemed more probable. This was supported by intensity statistics and was later verified by the final structure.

Three-dimensional intensities were collected with a scintillation counter on the PW 1100 diffractometer in

Table 1. *Crystal data for TMACXN*

Here and throughout this paper the e.s.d.'s are given in parentheses and refer to the last digit.

$C_{28}H_{51}NNiO_4S_6$	FW = 716.79
Monoclinic	Space group Cc
$a = 12.593$ (6) Å	$Z = 4$
$b = 17.776$ (8)	$F(000) = 1528$
$c = 16.589$ (6)	$\rho_{calc} = 1.283$ Mg m ⁻³
$\beta = 92.54$ (4)°	$\rho_{meas} = 1.261$
$V = 3709.85$ Å ³	$\mu = 0.879$ mm ⁻¹
	$\lambda(Mo K\alpha_1) = 0.70930$ Å

the $\theta/2\theta$ scan mode, using graphite-monochromatized Mo $K\alpha$ radiation. The intensities of 3877 reflexions in the θ range 3–20° were examined, measured and subsequently averaged to 1737 non-equivalent reflexions (maximum $h,k,l = 16, 22, \pm 21$). Of them 1269 with intensities greater than 2σ were considered as observed and included in all further calculations. Integrated intensities were converted to $|F_o|$ values in the usual way, using the special measurement treatment program *DATRED* (Main, 1970). Since μ is fairly small, no absorption correction was applied. For further calculations the programs of the *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and *XRAY* systems were used.

Structure determination and refinement

The structure was solved by direct phase determination with the *MULTAN* system. The phases of 300 strong reflexions were determined and on the resulting E map it was possible to locate 13 of the 40 non-hydrogen atoms in the asymmetric unit. A structure factor calculation at this stage, with all the reflexions and approximate individual isotropic temperature coefficients, gave $R = 0.207$. The remaining atoms were located by means of successive difference Fourier syntheses.

The structure was refined by full-matrix least-squares calculations. The atomic scattering factors for all the atoms and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). A single scale factor was used for the whole set of reflexion data.

Six cycles of refinement with all the non-hydrogen atoms, isotropic temperature coefficients and unit weights gave $R = 0.072$. Using anisotropic temperature coefficients and the weighting scheme $w = 1/\sigma^2(F)$, which proved to be the most suitable, the R factor was reduced to 0.063. In order to have a better ratio of the reflexions used to the number of parameters refined, 312 'less-than' reflexions, with $|F_c| > |F_o|$, were added to the set of the observed reflexions, thus increasing it to 1581. This slightly improved the standard deviations of the atomic parameters while the R factor remained unchanged. Then, the positions of the H atoms in the cyclohexane rings were calculated assuming a C–H bond length of 1.08 Å. A difference Fourier synthesis revealed most of the H atoms very near to their calculated positions. An attempt to include the H atoms in the refinement, however, proved unsuccessful. Hence, in the final stage of refinement the H atoms were kept fixed at their calculated positions, with their individual isotropic temperature coefficients equal to the equivalent isotropic temperature coefficients of the C atoms to which they are bonded (Hamilton, 1959). The final R factor was 0.060 ($R_w = 0.051$). The

positional and isotropic thermal parameters for the non-hydrogen atoms are given in Table 2 and those for the H atoms in Table 3. Interatomic distances and bond angles are given in Tables 4 and 5.*

Description of the structure and discussion

A clinographic projection of the asymmetric unit of TMACXN is given in Fig. 1. As in the cases of trimethylphenylammonium tris(*O*-ethyl dithio-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34051 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates and equivalent isotropic temperature factors for the non-hydrogen atoms in TMACXN

	x	y	z	B (Å ²)
Ni	0.2287	0.6553 (1)	0.6889	3.54
S(1)	0.2342 (4)	0.7168 (3)	0.8184 (3)	4.37
S(2)	0.0833 (4)	0.6038 (3)	0.7609 (3)	4.20
S(3)	0.1268 (4)	0.7501 (3)	0.6111 (3)	4.17
S(4)	0.1802 (4)	0.5989 (3)	0.5615 (3)	4.18
S(5)	0.4004 (4)	0.7021 (3)	0.6490 (3)	4.41
S(6)	0.3622 (4)	0.5571 (3)	0.7222 (3)	4.24
O(1)	0.0870 (9)	0.6703 (7)	0.9059 (7)	6.25
O(2)	0.0799 (8)	0.7004 (7)	0.4671 (6)	5.02
O(3)	0.5503 (8)	0.6013 (6)	0.6893 (7)	4.71
O(4)	0.1057 (16)	0.0460 (10)	0.3820 (10)	12.55
N	0.4189 (11)	0.4191 (7)	0.4878 (9)	5.12
C(1)	0.1275 (12)	0.6616 (10)	0.8338 (9)	4.36
C(2)	−0.0063 (15)	0.6255 (11)	0.9250 (13)	6.15
C(3)	0.0174 (17)	0.5824 (14)	1.0045 (17)	9.33
C(4)	−0.0805 (23)	0.5426 (15)	1.0319 (15)	10.01
C(5)	−0.1729 (18)	0.5895 (17)	1.0314 (14)	9.13
C(6)	−0.1997 (17)	0.6407 (14)	0.9593 (17)	10.26
C(7)	−0.1002 (14)	0.6823 (14)	0.9329 (14)	9.28
C(8)	0.1266 (10)	0.6837 (8)	0.5408 (8)	2.30
C(9)	0.0811 (14)	0.6478 (10)	0.3985 (9)	4.42
C(10)	−0.0080 (15)	0.6665 (10)	0.3367 (11)	5.44
C(11)	−0.0131 (16)	0.6087 (12)	0.2712 (11)	5.59
C(12)	0.0938 (22)	0.6160 (11)	0.2310 (13)	6.95
C(13)	0.1895 (15)	0.6026 (11)	0.2900 (11)	5.31
C(14)	0.1919 (16)	0.6581 (10)	0.3601 (11)	5.18
C(15)	0.4465 (13)	0.6218 (9)	0.6862 (10)	4.07
C(16)	0.6336 (14)	0.6516 (9)	0.6603 (11)	3.97
C(17)	0.6541 (18)	0.6260 (14)	0.5763 (15)	8.37
C(18)	0.7453 (22)	0.6716 (15)	0.5405 (15)	9.45
C(19)	0.8406 (19)	0.6688 (14)	0.5998 (23)	9.15
C(20)	0.8120 (17)	0.6967 (15)	0.6810 (17)	7.46
C(21)	0.7324 (16)	0.6375 (13)	0.7132 (11)	6.52
C(22)	0.3455 (18)	0.3707 (13)	0.5361 (14)	8.19
C(23)	0.3496 (14)	0.4718 (10)	0.4402 (12)	5.59
C(24)	0.4833 (17)	0.3746 (11)	0.4249 (13)	6.82
C(25)	0.4983 (17)	0.4537 (13)	0.5414 (11)	7.34
C(26)	0.0938 (24)	0.0858 (14)	0.3200 (11)	9.50
C(27)	0.0043 (22)	0.1410 (17)	0.2949 (20)	11.86
C(28)	0.1771 (22)	0.0750 (14)	0.2556 (15)	10.52

carbonato)nickelate(II) (D'Addario, 1970) and tetramethylammonium tris(*O*-isobutyl dithiocarbonato)nickelate(II) (Christidis & Rentzeperis, 1978) the characteristic feature of the tris(*O*-cyclohexyl dithiocarbonato)nickelate(II) anion in TMACXN (CXN anion in the following) is that the central Ni atom is surrounded by six S atoms at the vertices of a distorted octahedron, with all three cyclohexyl dithiocarbonato ligands as bidentates. The CXN anion, like the anions of the two structures above, has approximate trigonal symmetry, in contrast to the dithiocarbonates of some trivalent metals (Cr, Fe, Co) (Merlino & Sartori, 1971; Hoskins & Kelly, 1970; Merlino, 1969) with similar octahedral coordination of the central atom, which belong to space group $R\bar{3}$ and whose molecules possess strict trigonal symmetry.

In Table 6 various least-squares planes of the CXN anion and the acetone molecule are listed, together with the dihedral angles between them. The Ni atom lies on a plane with the atoms C(1), C(8) and C(15), approximately occupying the centre of the triangle formed by them. This plane, approximately parallel to (010), is prominent in the structure: all the atoms of the three

Table 3. Calculated atomic coordinates for the H atoms in TMACXN

	x	y	z
H1(C2)	-0.0314	0.5843	0.8791
H1(C3)	0.0803	0.5428	0.9953
H2(C3)	0.0455	0.6237	1.0497
H1(C4)	-0.0955	0.4957	0.9945
H2(C4)	-0.0612	0.5233	1.0944
H1(C5)	-0.2397	0.5539	1.0419
H2(C5)	-0.1631	0.6274	1.0856
H1(C6)	-0.2293	0.6057	0.9101
H2(C6)	-0.2598	0.6810	0.9742
H1(C7)	-0.1168	0.7106	0.8765
H2(C7)	-0.0773	0.7242	0.9787
H1(C9)	0.0766	0.5894	0.4172
H1(C10)	-0.0823	0.6681	0.3666
H2(C10)	0.0067	0.7206	0.3100
H1(C11)	-0.0239	0.5511	0.2939
H2(C11)	-0.0775	0.6222	0.2303
H1(C12)	0.0957	0.5739	0.1843
H2(C12)	0.0990	0.6708	0.2070
H1(C13)	0.1879	0.5456	0.3131
H2(C13)	0.2618	0.6096	0.2569
H1(C14)	0.2559	0.6445	0.4043
H2(C14)	0.2017	0.7149	0.3400
H1(C16)	0.6138	0.7113	0.6592
H1(C17)	0.6696	0.5677	0.5752
H2(C17)	0.5812	0.6372	0.5371
H1(C18)	0.7683	0.6463	0.4853
H2(C18)	0.7229	0.7291	0.5309
H1(C19)	0.8730	0.6124	0.6094
H2(C19)	0.9066	0.7049	0.5816
H1(C20)	0.8799	0.7021	0.7237
H2(C20)	0.7735	0.7514	0.6757
H1(C21)	0.7619	0.5811	0.7051
H2(C21)	0.7172	0.6464	0.7760

Table 4. Interatomic distances (Å) in TMACXN

NiS ₆ octahedron		Third <i>O</i> -cyclohexyl dithiocarbonato group	
Ni-S(1)	2.409 (5)	S(5)-C(15)	1.65 (2)
Ni-S(2)	2.411 (5)	S(6)-C(15)	1.69 (2)
Ni-S(3)	2.450 (5)	C(15)-O(3)	1.36 (2)
Ni-S(4)	2.393 (5)	O(3)-C(16)	1.47 (2)
Ni-S(5)	2.434 (5)	C(16)-C(17)	1.50 (3)
Ni-S(6)	2.469 (5)	C(17)-C(18)	1.55 (4)
		C(18)-C(19)	1.52 (4)
		C(19)-C(20)	1.49 (5)
		C(20)-C(21)	1.56 (3)
		C(21)-C(16)	1.51 (3)
		Tetramethylammonium cation	
		N-C(22)	1.52 (3)
		N-C(23)	1.48 (2)
		N-C(24)	1.57 (3)
		N-C(25)	1.45 (2)
		Acetone molecule	
		C(26)-C(27)	1.53 (4)
		C(26)-C(28)	1.54 (4)
		C(26)-O(4)	1.25 (3)

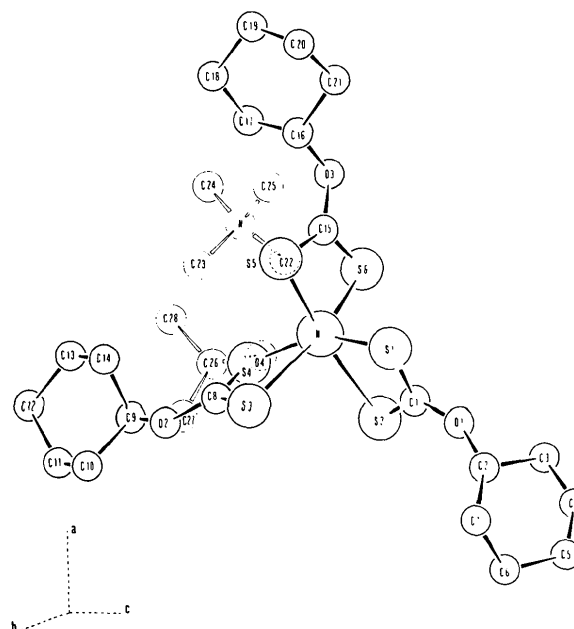


Fig. 1. Clinographic projection of the asymmetric unit of TMACXN.

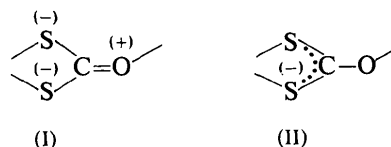
ligands lie within a layer, approximately 4 Å thick, parallel to this plane.

As expected from other dithiocarbonate structures, all three S₂CO groups are planar to a very good approximation. Since the Ni atoms do not deviate from these planes by more than 0.15 Å, the three NiS₂CO systems may be considered as virtually planar. The angles these planes form with one another are 79.7, 85.5 and 85.7°, *i.e.* they are almost mutually perpendicular.

The general features of the CXN anion are normal. The Ni–S distances range from 2.393 to 2.469 Å and are in very good agreement with the corresponding distances 2.27–2.47 Å, found in the tris(*O*-ethyl dithiocarbonato)nickelate(II) anion (D'Addario, 1970), and 2.385–2.478 Å, found in the tris(*O*-isobutyl dithiocarbonato)nickelate(II) anion (Christidis & Rentzeperis, 1978). Assuming an octahedral covalent radius for Ni^{II} of 1.39 Å and for S of 1.04 Å (Pauling, 1960), we find a distance Ni–S 2.43 Å, which is in excellent agreement with the observed mean Ni–S distance of 2.428 Å.

The mean values for S–C and C–O in the S₂CO groups are 1.67 and 1.35 Å respectively, and compare well with the corresponding values of the previously mentioned dithiocarbonates. These values indicate, of

course, partial double-bond character in the S₂CO groups. Assuming the usually accepted resonance structures for the dithiocarbonato ligand,



the calculated contributions according to the valence bond theory (Pauling, 1960) are 15% for structure (I) and 85% for structure (II). These are identical to the corresponding values, found in tetramethylammonium tris(*O*-isobutyl dithiocarbonato)nickelate(II) (Christidis & Rentzeperis, 1978). For comparison with other dithiocarbonates and dithiocarbamates, see this last paper.

Table 6. *Least-squares planes in TMACXN, with displacements of atoms from the planes (Å)*

The equation for a plane is in the form $AX + BY + CZ = D$ and refers to an orthogonal system of axes, with $X \parallel a$, Y in the ab plane, $Z \parallel c^*$ and D , the distance of the plane from the origin, in Å. Asterisks indicate atoms not included in the calculation of the plane. Mean estimated standard deviations of the atoms defining a plane are given in parentheses following the distance of the first atom.

Table 5. *Bond angles (°) in TMACXN*

NiS ₆ octahedron		Second <i>O</i> -cyclohexyl dithiocarbonato group	
S(1)–Ni–S(2)	73.9 (0.2)	S(3)–C(8)–S(4)	120.4 (0.8)
S(1)–Ni–S(3)	98.7 (0.2)	S(3)–C(8)–O(2)	117.6 (1.1)
S(1)–Ni–S(4)	166.8 (0.2)	S(4)–C(8)–O(2)	122.1 (1.1)
S(1)–Ni–S(5)	95.6 (0.2)	C(8)–O(2)–C(9)	122.4 (1.2)
S(1)–Ni–S(6)	97.4 (0.2)	O(2)–C(9)–C(10)	110.5 (1.4)
S(2)–Ni–S(3)	97.5 (0.2)	O(2)–C(9)–C(14)	106.3 (1.3)
S(2)–Ni–S(4)	96.2 (0.2)	C(9)–C(10)–C(11)	110.3 (1.5)
S(2)–Ni–S(5)	165.3 (0.2)	C(10)–C(11)–C(12)	104.3 (1.6)
S(2)–Ni–S(6)	98.4 (0.2)	C(11)–C(12)–C(13)	112.9 (1.6)
S(3)–Ni–S(4)	73.5 (0.2)	C(12)–C(13)–C(14)	112.0 (1.6)
S(3)–Ni–S(5)	94.2 (0.2)	C(13)–C(14)–C(9)	104.3 (1.4)
S(3)–Ni–S(6)	160.0 (0.2)	C(14)–C(9)–C(10)	110.1 (1.4)
S(4)–Ni–S(5)	95.7 (0.2)	Third <i>O</i> -cyclohexyl dithiocarbonato group	
S(4)–Ni–S(6)	92.7 (0.2)	S(5)–C(15)–S(6)	120.2 (1.0)
S(5)–Ni–S(6)	72.4 (0.2)	S(5)–C(15)–O(3)	124.7 (1.2)
First <i>O</i> -cyclohexyl dithiocarbonato group		S(6)–C(15)–O(3)	115.0 (1.1)
S(1)–C(1)–S(2)	119.4 (0.9)	C(15)–O(3)–C(16)	121.6 (1.2)
S(1)–C(1)–O(1)	114.0 (1.2)	O(3)–C(16)–C(17)	105.9 (1.4)
S(2)–C(1)–O(1)	126.6 (1.2)	O(3)–C(16)–C(21)	106.8 (1.4)
C(1)–O(1)–C(2)	118.3 (1.4)	C(16)–C(17)–C(18)	111.1 (1.9)
O(1)–C(2)–C(3)	109.1 (1.5)	C(17)–C(18)–C(19)	108.3 (2.1)
O(1)–C(2)–C(7)	106.4 (1.5)	C(18)–C(19)–C(20)	110.9 (2.0)
C(2)–C(3)–C(4)	111.1 (1.8)	C(19)–C(20)–C(21)	105.6 (2.0)
C(3)–C(4)–C(5)	113.6 (2.3)	C(20)–C(21)–C(16)	102.4 (1.7)
C(4)–C(5)–C(6)	120.2 (2.1)	C(21)–C(16)–C(17)	108.6 (1.6)
C(5)–C(6)–C(7)	110.8 (1.8)	Tetramethylammonium cation	
C(6)–C(7)–C(2)	110.0 (1.9)	C(22)–N–C(23)	106.3 (1.4)
C(7)–C(2)–C(3)	111.6 (1.8)	C(22)–N–C(24)	114.2 (1.4)
Acetone molecule		C(22)–N–C(25)	109.7 (1.5)
O(4)–C(26)–C(27)	129.9 (2.5)	C(23)–N–C(24)	106.0 (1.4)
O(4)–C(26)–C(28)	116.0 (2.3)	C(23)–N–C(25)	115.7 (1.4)
C(27)–C(26)–C(28)	113.9 (2.0)	C(24)–N–C(25)	105.1 (1.4)

Plane I: central plane formed by Ni and C atoms

$$0.21864X + 0.97182Y + 0.08814Z = 12.85877$$

Ni	–0.013 (9)	O(1)*	0.137
C(1)	0.004	O(2)*	0.067
C(8)	0.004	O(3)*	–0.060
C(15)	0.004		

Plane II: first dithiocarbonato group

$$–0.58867X + 0.71979Y – 0.36793Z = 2.79813$$

S(1)	0.001 (1)	O(1)	0.001
S(2)	0.002	Ni*	–0.011
C(1)	–0.002	C(2)*	0.011

Plane III: second dithiocarbonato group

$$0.89449X + 0.32871Y – 0.30305Z = 2.34231$$

S(3)	–0.002 (5)	O(2)	–0.003
S(4)	–0.002	Ni*	0.151
C(8)	0.008	C(9)*	0.094

Plane IV: third dithiocarbonato group

$$0.07147X + 0.41261Y + 0.90810Z = 15.24536$$

S(5)	–0.003 (5)	O(3)	–0.003
S(6)	–0.002	Ni*	0.098
C(15)	0.008	C(16)*	0.006

Plane V: acetone molecule

$$0.51847X + 0.74126Y + 0.42628Z = 3.85867$$

O(4)	–0.009 (15)	C(27)	–0.007
C(26)	0.022	C(28)	–0.006

Dihedral angles between planes (°)

I–II	57.4	II–III	79.7	III–IV	85.7	IV–V	43.1
I–III	60.8	II–IV	85.5	III–V	54.7		
I–IV	60.2	II–V	85.9				
I–V	29.4						

The cyclohexane rings are in the chair form. The mean bond distances in the three cyclohexane rings are 1.52, 1.53 and 1.52 Å, while the corresponding mean bond angles and mean torsion angles are respectively 112.9, 109.0, 107.8° and 50.0, 61.1, 63.1°. These values compare well with corresponding values found in other compounds containing cyclohexane rings, such as *cis*-4-aminomethylcyclohexanecarboxylic acid hydrobromide (Groth & Hassel, 1965). The determined torsion angles in TMACXN, however, indicate that the first cyclohexane ring is somewhat flatter than the normal cyclohexane ring (mean torsion angle = 55.2°), while the other two are slightly more puckered.

The tetramethylammonium cation appears normal. The determined mean bond distance 1.51 Å agrees well with the accepted N—C single-bond distance 1.495 Å (*International Tables for X-ray Crystallography*, 1968) while the individual bond angles differ from the ideal tetrahedral value by no more than 6.2°. Also, the features of the acetone molecule are normal. The molecule is strictly planar, with mean C—C distance 1.535 Å and C=O distance 1.25 Å, which agree well with the corresponding values 1.541 and 1.23 Å, given in *International Tables for X-ray Crystallography* (1968).

The molecular packing of the structure is shown in Fig. 2. The roughly planar anions form layers approximately parallel to (010), being interconnected by the tetramethylammonium cations and the acetone molecules which are distributed both within the layers and also between them. Intermolecular distances which are shorter than the corresponding van der Waals radii are given in Table 7.

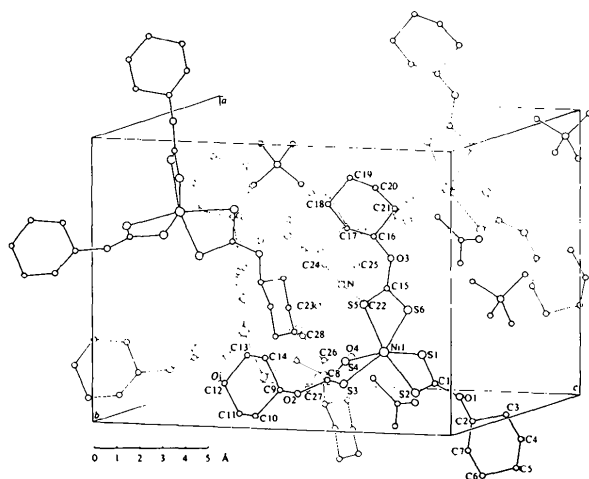


Fig. 2. Clinographic projection of TMACXN showing the molecular packing.

Table 7. Intermolecular distances (Å) in TMACXN, shorter than or equal to the sum of the corresponding van der Waals radii

S(6)···C(13) ^{VI}	3.78 (2)	C(2)···C(12) ^{II}	3.88 (3)
S(6)···C(23) ^{VI}	3.66 (2)	C(10)···C(24) ^{IV}	3.98 (3)
S(6)···C(24) ^{VI}	3.83 (2)	C(11)···C(28) ^{IV}	3.94 (3)
O(2)···C(24) ^{IV}	3.39 (2)	C(18)···C(22) ^{III}	3.76 (3)
O(4)···C(17) ^V	3.55 (3)	C(20)···C(22) ^{III}	3.95 (4)
O(4)···C(25) ^V	3.44 (3)	C(21)···C(28) ^{VI}	3.91 (3)

Symmetry code

(I)	$x,$	$y,$	z	(V)	$-\frac{1}{2} + x,$	$-\frac{1}{2} + y,$	z
(II)	$x,$	$y,$	$1 + z$	(VI)	$x,$	$1 - y,$	$\frac{1}{2} + z$
(III)	$\frac{1}{2} + x,$	$\frac{1}{2} + y,$	z	(VII)	$\frac{1}{2} + x,$	$\frac{1}{2} - y,$	$\frac{1}{2} + z$
(IV)	$-\frac{1}{2} + x,$	$\frac{1}{2} + y,$	z				

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