

References

- BARNES, J. C., IBALL, J. & WEAKLEY, T. J. R. (1975). *Acta Cryst.* **B31**, 1435–1437.
- BRADDOCK, P. D., CONNORS, T. A., JONES, M., KHOKHAR, A. R., MELZACK, D. H. & TOBE, M. L. (1975). *Chem. Biol. Interact.* **11**, 145–162.
- COLAMARINO, P. & ORIOLI, P. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1656–1659.
- HARDER, H. C. & ROSENBERG, B. (1970). *Cancer Res.* **6**, 207–216.
- IBALL, J., MACDOUGALL, M. & SCRIMGEOUR, S. (1975). *Acta Cryst.* **B31**, 1672–1674.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- LAUHER, J. W. & IBERS, J. A. (1975). *Inorg. Chem.* **14**, 640–645.
- MACQUET, J. P. & THEOPHANIDES, T. (1975). *Biopolymers*, **14**, 781–799.
- MILLARD, M. M., MACQUET, J. P. & THEOPHANIDES, T. (1975). *Biochim. Biophys. Acta*, **402**, 166–170.
- MUNCHAUSEN, L. L. & RAHN, R. O. (1975). *Biochim. Biophys. Acta*, **414**, 242–255.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- ROSENBERG, B., VAN CAMP, L., TROSKO, J. E. & MANSOUR, V. H. (1969). *Nature (London)*, **222**, 385–386.
- SHELDRIK, G. (1976). *SHELX 76* system of computing programs. Univ. of Cambridge, England.
- TAMBURRO, A. M., CELOTTI, L., FURLAN, D. & GUANTIERI, V. (1977). *Chem. Biol. Interact.* **16**, 1–11.

Acta Cryst. (1978). **B34**, 2141–2146

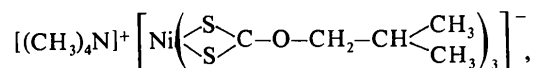
The Crystal Structure of Tetramethylammonium Tris(*O*-isobutyl dithiocarbonato)nickelate(II)

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The crystal structure of the title compound,



has been determined from three-dimensional intensities, measured on a computer-controlled Philips PW 1100 single-crystal diffractometer (1898 observed reflexions). The crystals are monoclinic, space group $P2_1/c$, with $a = 11.0536$ (6), $b = 19.3833$ (9), $c = 15.5217$ (9) Å, $\beta = 117.89$ (1)°, and $Z = 4$. 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 $R = 0.050$ ($R_w = 0.041$). 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 2.385–2.478 Å, whereas in the dithiocarbonate ligands the C–S distances range between 1.657 and 1.683 Å and C–O distances between 1.342 and 1.356 Å. The roughly planar anions form layers approximately parallel to (104), and are interconnected by the tetramethylammonium cations, which are distributed both in and between the layers.

Introduction

Ionic tris(dithiocarbonato) complexes of bivalent metals have been of considerable interest in the past decade. So far as we know, of the Ni^{II} complexes only trimethylphenylammonium tris(*O*-ethyl dithiocarbonato)nickelate(II) (D'Addario, 1970) has been structurally analysed.

Since a number of new compounds, progressively

more heavily substituted, have recently been prepared at the Inorganic Chemistry Laboratory of the University of Thessaloniki (Hatzikostas & Manoussakis, 1977), it was considered advisable to carry out a systematic structure investigation of certain selected members of the group. The structure of tetramethylammonium tris(*O*-isobutyl dithiocarbonato)nickelate(II) (TMAIXN hereafter) is the first to be determined.

Experimental

Pure, green crystals of TMAIXN were kindly provided by Professor G. Manoussakis and Mr C. Hatzikostas of the Inorganic Chemistry Laboratory. The selected crystal, a prism with dimensions $0.56 \times 0.16 \times 0.08$ mm, was centred on our computer-controlled Philips PW 1100 four-circle single-crystal diffractometer. Accurate cell parameters were obtained from direct measurement on the diffractometer of the θ angles of 173 reflexions with large θ values. The measurements were subsequently 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.

Three-dimensional intensity data were collected with a scintillation counter on the PW 1100 diffractometer in the $\theta/2\theta$ scan mode, using Mo $K\alpha$ radiation monochromatized with a graphite monochromator. The intensities of 6095 reflexions in the range $\theta = 3\text{--}20^\circ$ were examined and measured and subsequently averaged to give 2733 non-equivalent reflexions (maximum $hkl = 10, 18, \pm 14$). Of these, 1898 with intensities greater than 2σ were considered as observed and included in all further computations. 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 16 of the 30 non-hydrogen atoms in the asymmetric unit. A structure factor calculation at this stage, with all the reflexions

Table 1. *Crystal data for TMAIXN*

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

$C_{19}H_{39}NNiO_3S_6$
 Monoclinic
 $a = 11.0536$ (6) Å
 $b = 19.3833$ (9)
 $c = 15.5217$ (9)
 $\beta = 117.89$ (1)°
 $V = 2939.33$ Å³

FW 580.60
 Space group $P2_1/c$
 $Z = 4$
 $F(000) = 1232$
 $\rho_{\text{calc}} = 1.305$ g cm⁻³
 $\rho_{\text{meas}} = 1.342$
 $\mu = 10.84$ cm⁻¹
 $\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å

and approximate individual isotropic temperature coefficients, gave $R = 0.203$. The remaining atoms were located by means of a difference Fourier synthesis. 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 reduced R to 0.095. However, in one of the isobutyl groups of the dithiocarbonate anion the terminal C atom, labelled C(9) in Fig. 1, showed an extremely high temperature factor. This was evidence that this atom might display disorder. In fact, a difference Fourier map (Fig. 2) calculated with all the atoms except those of the

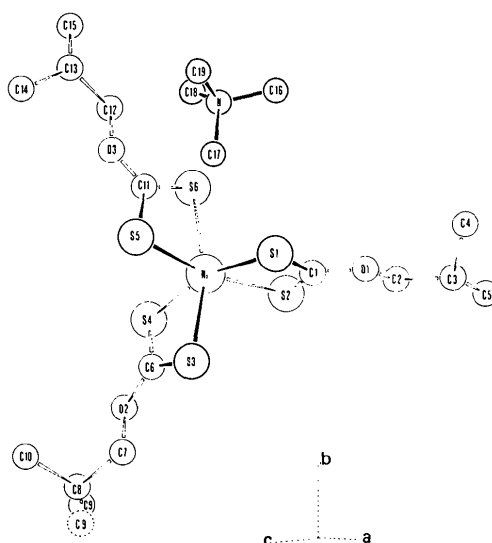


Fig. 1. Clinographic projection of the asymmetric unit of TMAIXN.

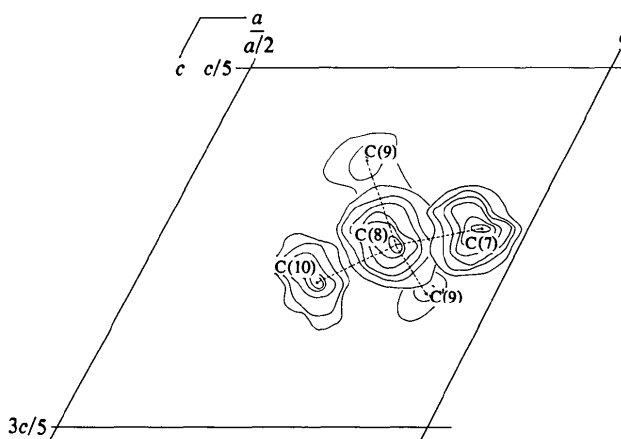


Fig. 2. Projection of the peaks of the three-dimensional difference Fourier synthesis on (010), calculated with all the non-hydrogen atoms except those of the disordered isobutyl group. Contours are at intervals of $0.4 \text{ e } \text{Å}^{-3}$; threshold at $0.4 \text{ e } \text{Å}^{-3}$.

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

	x	y	z	B (Å ²)
Ni	0.0277 (1)	0.3732 (1)	0.2833 (1)	3.8
S(1)	0.2664 (2)	0.4108 (1)	0.3435 (2)	5.3
S(2)	0.0935 (2)	0.3411 (1)	0.1617 (1)	4.5
S(3)	0.0829 (2)	0.2635 (1)	0.3699 (2)	4.6
S(4)	-0.1824 (2)	0.3058 (1)	0.2164 (2)	4.3
S(5)	-0.0161 (2)	0.4321 (1)	0.4008 (2)	5.3
S(6)	-0.0882 (2)	0.4828 (1)	0.2067 (2)	5.0
O(1)	0.3463 (5)	0.3844 (3)	0.2152 (4)	5.5
O(2)	-0.1470 (5)	0.1915 (3)	0.3083 (4)	5.4
O(3)	-0.1551 (5)	0.5421 (3)	0.3337 (4)	5.7
N	0.2873 (6)	0.6268 (4)	0.4929 (5)	5.7
C(1)	0.2411 (8)	0.3781 (4)	0.2359 (5)	4.4
C(2)	0.3241 (8)	0.3618 (5)	0.1178 (6)	6.1
C(3)	0.4571 (9)	0.3704 (6)	0.1176 (6)	7.1
C(4)	0.5133 (10)	0.4414 (5)	0.1360 (9)	9.7
C(5)	0.4381 (10)	0.3409 (6)	0.0203 (7)	9.2
C(6)	-0.0829 (7)	0.2491 (4)	0.3009 (5)	4.1
C(7)	-0.0697 (8)	0.1405 (4)	0.3830 (6)	5.6
C(8)	-0.1742 (10)	0.0906 (5)	0.3894 (9)	7.9
C(9)	-0.2598 (22)	0.0559 (10)	0.3045 (15)	8.0
C'(9)	-0.1015 (19)	0.0314 (10)	0.4482 (13)	7.0
C(10)	-0.2547 (10)	0.1311 (6)	0.4320 (8)	9.1
C(11)	-0.0916 (7)	0.4909 (4)	0.3126 (5)	4.4
C(12)	-0.2991 (8)	0.5942 (4)	0.2615 (6)	5.3
C(13)	-0.2819 (10)	0.6492 (5)	0.3051 (7)	7.9
C(14)	-0.3384 (15)	0.6267 (7)	0.3650 (10)	15.7
C(15)	-0.3677 (10)	0.6989 (5)	0.2271 (7)	6.9
C(16)	0.3774 (11)	0.6423 (8)	0.4461 (10)	14.9
C(17)	0.3201 (12)	0.5581 (6)	0.5402 (10)	11.3
C(18)	0.1421 (10)	0.6327 (8)	0.4199 (9)	12.2
C(19)	0.3209 (16)	0.6734 (8)	0.5715 (12)	15.6

isobutyl group in question revealed for C(9) two peaks of approximately equal height. Similar situations, where one or more of the terminal C atoms of the alkyl chain exhibit disorder, have been confirmed in several compounds, e.g. the tris(*O*-ethyl dithiocarbonato)-tellurate(II) anion (Hoskins & Pannan, 1975).

A refinement cycle with isotropic temperature factors and population parameters of 0.5 for C(9) and C'(9) gave $R = 0.090$ and reasonable temperature coefficients. Further refinement with anisotropic temperature factors and the weighting scheme $w = 1/\sigma^2(F)$, which best suited the data, reduced R to 0.057. The population parameters of C(9) and C'(9) were not considered as separate variables in the least-squares refinement, but attempts were made to refine with different sets of population parameters. The best results were obtained with the value 0.5 for each of the atoms C(9) and C'(9). Next, the H atoms were located using the XRAY system. Most of the positions calculated in this way were found to correspond to maxima on the difference Fourier map. However, the H atoms of the tetramethylammonium groups and of those bonded to C(8), C(9) and C'(9) could not be located, due to the

Table 3. Atomic coordinates and isotropic temperature factors for the hydrogen atoms in TMAIXN

	x	y	z	B (Å ²)
H1(C2)	0.246 (8)	0.405 (4)	0.069 (6)	7.1 (2.5)
H2(C2)	0.277 (9)	0.306 (5)	0.105 (7)	10.0 (3.0)
H(C3)	0.508 (8)	0.333 (4)	0.175 (6)	7.1 (2.5)
H1(C4)	0.509 (11)	0.458 (6)	0.191 (9)	13.6 (3.9)
H2(C4)	0.456 (13)	0.482 (7)	0.087 (10)	15.5 (4.1)
H3(C4)	0.619 (9)	0.436 (5)	0.139 (7)	8.5 (2.7)
H1(C5)	0.352 (9)	0.375 (5)	-0.034 (6)	7.6 (2.5)
H2(C5)	0.510 (10)	0.357 (5)	0.010 (7)	8.3 (2.7)
H3(C5)	0.387 (9)	0.287 (5)	-0.004 (7)	9.8 (2.9)
H1(C7)	-0.010 (8)	0.123 (4)	0.353 (6)	5.5 (2.2)
H2(C7)	-0.004 (7)	0.157 (4)	0.446 (6)	5.3 (2.2)
H1(C10)	-0.323 (12)	0.079 (6)	0.436 (9)	15.1 (3.9)
H2(C10)	-0.337 (10)	0.152 (5)	0.366 (7)	9.2 (2.8)
H3(C10)	-0.197 (10)	0.147 (5)	0.492 (7)	10.6 (3.2)
H1(C12)	-0.308 (10)	0.557 (5)	0.203 (7)	10.7 (3.1)
H2(C12)	-0.156 (9)	0.626 (5)	0.242 (7)	8.7 (2.7)
H(C13)	-0.199 (7)	0.675 (4)	0.388 (5)	4.7 (2.1)
H1(C14)	-0.288 (10)	0.600 (5)	0.415 (7)	9.2 (3.0)
H2(C14)	-0.416 (12)	0.607 (7)	0.302 (10)	15.2 (4.3)
H3(C14)	-0.398 (9)	0.664 (5)	0.380 (7)	7.5 (2.5)
H1(C15)	-0.453 (7)	0.670 (4)	0.174 (5)	4.5 (2.0)
H2(C15)	-0.409 (10)	0.741 (5)	0.248 (7)	9.5 (2.9)
H3(C15)	-0.315 (11)	0.723 (6)	0.194 (8)	12.2 (3.4)

Table 4. Interatomic distances (Å) in TMAIXN

NiS ₆ octahedron		Third <i>O</i> -isobutyl dithiocarbonato group	
Ni-S(1)	2.461 (2)	S(5)-C(11)	1.675 (7)
Ni-S(2)	2.400 (3)	S(6)-C(11)	1.668 (9)
Ni-S(3)	2.436 (2)	C(11)-O(3)	1.342 (10)
Ni-S(4)	2.433 (2)	O(3)-C(12)	1.444 (9)
Ni-S(5)	2.385 (3)	C(12)-C(13)	1.52 (2)
Ni-S(6)	2.478 (2)	C(3)-C(14)	1.41 (2)
		C(13)-C(15)	1.49 (1)
First <i>O</i> -isobutyl dithiocarbonato group		Tetramethylammonium cation	
S(1)-C(1)	1.683 (9)	N-C(16)	1.51 (2)
S(2)-C(1)	1.657 (7)	N-C(17)	1.48 (1)
C(1)-O(1)	1.348 (12)	N-C(18)	1.47 (1)
O(1)-C(2)	1.480 (11)	N-C(19)	1.42 (2)
C(2)-C(3)	1.48 (1)		
C(3)-C(4)	1.48 (2)		
C(3)-C(5)	1.53 (2)		
Second <i>O</i> -isobutyl dithiocarbonato group			
S(3)-C(6)	1.658 (7)		
S(4)-C(6)	1.670 (7)		
C(6)-O(2)	1.356 (10)		
O(2)-C(7)	1.457 (9)		
C(7)-C(8)	1.55 (2)		
C(8)-C(9)	1.38 (2)		
C(8)-C'(9)	1.45 (2)		
C(8)-C(10)	1.55 (2)		

large temperature coefficients of the C atoms and the disordered state of C(9) and C'(9). Six further cycles of refinement with anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the H atoms gave a final R factor of 0.050 ($R_w = 0.041$), while the average shift/error at convergence was 0.19.

Table 5. Bond angles ($^\circ$) in TMAIXN

NiS ₆ octahedron		First <i>O</i> -isobutyl dithiocarbonato group		Third <i>O</i> -isobutyl dithiocarbonato group	
S(1)—Ni—S(2)	73.15 (0.08)	S(1)—C(1)—S(2)	120.3 (0.6)	S(5)—C(11)—S(6)	120.5 (0.5)
S(1)—Ni—S(3)	95.83 (0.08)	S(1)—C(1)—O(1)	116.2 (0.5)	S(5)—C(11)—O(3)	114.9 (0.6)
S(1)—Ni—S(4)	163.85 (0.09)	S(2)—C(1)—O(1)	123.5 (0.6)	S(6)—C(11)—O(3)	124.5 (0.5)
S(1)—Ni—S(5)	97.62 (0.09)	C(1)—O(1)—C(2)	117.8 (0.5)	C(11)—O(3)—C(12)	119.8 (0.7)
S(1)—Ni—S(6)	98.63 (0.08)	O(1)—C(2)—C(3)	106.2 (0.6)	O(3)—C(12)—C(13)	109.9 (0.7)
S(2)—Ni—S(3)	96.78 (0.09)	C(2)—C(3)—C(4)	115.5 (1.0)	C(12)—C(13)—C(14)	117.2 (1.0)
S(2)—Ni—S(4)	96.05 (0.09)	C(2)—C(3)—C(5)	106.4 (0.7)	C(12)—C(13)—C(15)	108.9 (0.9)
S(2)—Ni—S(5)	165.86 (0.09)	C(4)—C(3)—C(5)	112.8 (1.0)	C(14)—C(13)—C(15)	115.2 (1.1)
S(2)—Ni—S(6)	97.12 (0.09)				
S(3)—Ni—S(4)	73.12 (0.07)	Second <i>O</i> -isobutyl dithiocarbonato group		Tetramethylammonium	
S(3)—Ni—S(5)	94.79 (0.09)	S(3)—C(6)—S(4)	121.3 (0.5)	C(16)—N—C(17)	110.7 (1.0)
S(3)—Ni—S(6)	162.31 (0.11)	S(3)—C(6)—O(2)	123.2 (0.5)	C(16)—N—C(18)	109.9 (0.9)
S(4)—Ni—S(5)	95.07 (0.09)	C(4)—C(6)—O(2)	115.5 (0.5)	C(16)—N—C(19)	108.7 (1.1)
S(4)—Ni—S(6)	94.56 (0.07)	C(6)—O(2)—C(7)	119.4 (0.5)	C(17)—N—C(18)	112.1 (0.9)
S(5)—Ni—S(6)	73.28 (0.08)	O(2)—C(7)—C(8)	107.3 (0.6)	C(17)—N—C(19)	104.0 (0.9)
		C(7)—C(8)—C(9)	116.2 (1.5)	C(18)—N—C(19)	111.4 (1.0)
		C(7)—C(8)—C'(9)	108.9 (1.1)		
		C(7)—C(8)—C(10)	107.7 (0.8)		
		C(9)—C(8)—C'(9)	98.4 (1.2)		
		C(9)—C(8)—C(10)	112.4 (1.3)		
		C'(9)—C(8)—C(10)	113.1 (1.4)		

The final 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 TMAIXN is given in Fig. 1. The characteristic feature of the tris(*O*-isobutyl dithiocarbonato)nickelate(II) anion (IXN anion hereafter) is that the central Ni atom is surrounded by six S atoms at the vertices of a distorted octahedron, with all three *O*-isobutyl dithiocarbonato ligands bidentate. A similar configuration has been found in the structure of trimethylphenylammonium tris(*O*-ethyl dithiocarbonato)nickelate(II) (D'Addario, 1970) and in the structures of Cr^{III}, Fe^{III} and Co^{III} tris(*O*-ethyl dithiocarbonates) (Merlino & Sartori, 1971; Hoskins & Kelly, 1970; Merlino, 1969). Unlike the three latter structures, however, which belong to space group $R\bar{3}$ and whose molecules possess strictly trigonal symmetry, in the present IXN anion this symmetry is only approximately retained.

In Table 6 are listed various least-squares planes of the IXN anion, together with the dihedral angles

between them. The Ni atom lies on a plane with the atoms C(1), C(6) and C(11), approximately occupying the centre of the triangle formed by them. This plane, parallel to **b** and very nearly parallel to (104), is prominent in the structure: all the atoms of the three ligands lie within a layer, approximately 4 Å thick, parallel to this plane.

As expected from other xanthate 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 0.196 Å, the three NiS₂CO systems may be considered as virtually planar. The angles these planes form with one another are 77.9, 79.9 and 86.7°, *i.e.* they are almost mutually perpendicular. The general features of the IXN anion are normal. The Ni—S distances range from 2.385 to 2.478 Å and are in very good agreement with the corresponding distances, 2.37–2.47 Å, found in the tris(*O*-ethyl dithiocarbonato)nickelate(II) anion (D'Addario, 1970). They are considerably longer than those (2.23–2.24 Å) determined in Ni^{II} bis(*O*-ethyl dithiocarbonate) (Franzini, 1963), where, however, the Ni atom has planar fourfold coordination. Assuming octahedral covalent radii of 1.39 Å for Ni^{II} and 1.04 Å for S (Pauling, 1960), we find a Ni—S distance of 2.43 Å, which is in excellent agreement with the observed mean Ni—S distance of 2.432 Å.

The mean values for S—C and C—O in the S₂CO groups are 1.669 and 1.349 Å, respectively, and these compare well with values found in the other dithiocarbonates mentioned above. The values indicate partial double-bond character in the group. The contributions

* Lists of structure factors, anisotropic thermal parameters and bond distances and bond angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33443 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

The equation for a plane is in the form $AX + BY + CZ = D$ and refers to orthogonal axes. The coordinates X , Y and Z are expressed in Å; D is the distance of the plane from the origin. 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.

Plane I: central plane formed by Ni and C atoms

$$0.22898X - 0.02447Y + 0.97312Z = 3.19218$$

Ni	0.012 (8)	O(1)*	0.017
C(1)	-0.004	O(2)*	-0.051
C(6)	-0.004	O(3)*	0.059
C(11)	-0.004	C(14)*	-0.080

Plane II: first dithiocarbonato group

$$-0.17473X + 0.88250Y - 0.43665Z = 4.88970$$

S(1)	0.001 (1)	Ni*	0.103
S(2)	0.001	C(2)*	0.118
C(1)	-0.002	C(3)*	0.008
O(1)	0.001	C(4)*	1.028
		C(5)*	0.000

Plane III: second dithiocarbonato group

$$-0.57746X + 0.45700Y + 0.67653Z = 6.78908$$

S(3)	0.000 (0)	Ni*	0.156
S(4)	0.000	C(7)*	0.061
C(6)	0.000	C(8)*	0.371
O(2)	0.000	C(9)*	-0.533
		C'(9)*	0.176
		C(10)*	1.819

Plane IV: third dithiocarbonato group

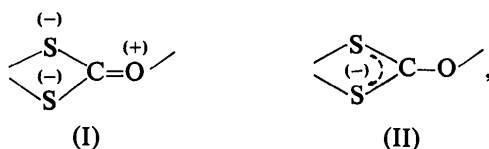
$$0.75938X + 0.53395Y + 0.37180Z = 4.17409$$

S(5)	-0.003 (6)	Ni*	-0.196
S(6)	-0.003	C(12)*	-0.056
C(11)	0.009	C(13)*	0.054
O(3)	-0.003	C(14)*	-0.679
		C(15)*	-0.121

Dihedral angles between planes (°)

I \wedge II	60.9	II \wedge III	77.9	III \wedge IV	86.7
I \wedge III	59.0	II \wedge IV	79.9		
I \wedge IV	58.5				

of the usually assumed resonance structures for the dithiocarbonato ligand,



calculated according to the valence-bond theory (Pauling, 1960), are: 15% for structure (I) and 85% for structure (II). These are close to the values of 13 and 87% found by Merlino (1969) for Co^{III} tris(*O*-ethyl

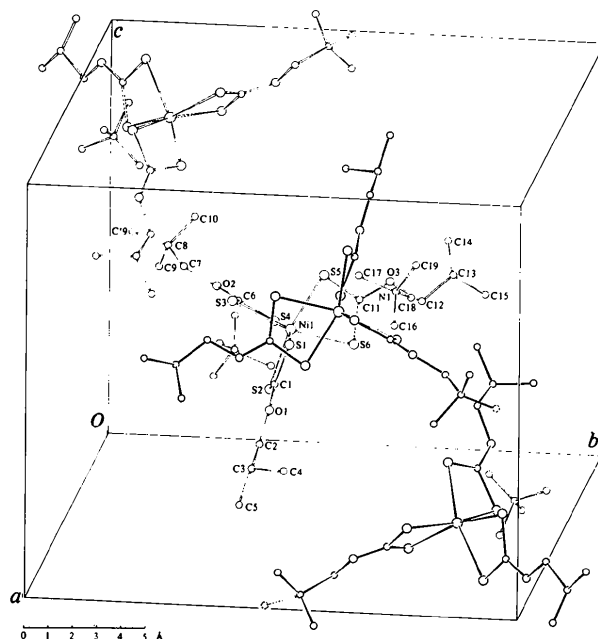


Fig. 3. Clinographic projection of TMAIXN showing the molecular packing.

dithiocarbonato). These are somewhat greater than the values of 9 and 91% calculated from the distances given by Franzini (1963) for the four-coordinated Ni^{II} bis(*O*-ethyl dithiocarbonato). However, they are less than in nickel dialkyldithiocarbonates, where, for example, in the case of Ni^{II} bis(*N,N*-di-*n*-propyldithiocarbonato) (Peyronel & Pignedoli, 1967) the resonance structure $\cdots\text{S}_2\text{C}=\text{NR}_2$ contributes 65%. It is once more confirmed that the form $\cdots\text{S}_2\text{C}=\text{OR}$ makes a minor contribution to the structure of dithiocarbonates compared to the contribution of the form $\cdots\text{S}_2\text{C}=\text{NR}_2$ to the structure of dialkyldithiocarbonates (Chatt, Duncanson & Venanzi, 1956).

As expected, the amplitudes of the thermal motion of the atoms in the *O*-isobutyl dithiocarbonato groups (Table 2) increase towards the end of each chain. This indicates, of course, that the 'free' ends of the dithiocarbonato ligands can move more freely from the ends bonded to the heavy atom.

The very short bond distance of 1.41 Å between C(13) and C(14) may be attributed to the abnormally large thermal motion of C(14). The other short interatomic distance between C(8) and C(9) (1.38 Å) may be attributed to the disorder of C(9). The tetramethylammonium cation appears normal. The mean C—N bond distance determined (1.47 Å) agrees well with the usually accepted N—C single-bond distance of 1.495 Å (*International Tables for X-ray Crystallography*, 1968). The bond angles differ from their ideal value of 109.47° by no more than 5.5° . The temperature factors of the four C atoms are very large compared to

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

S(1)...C(9) ^{VI}	3.61 (2)	C(9)...C(16) ^{VII}	3.86 (3)
S(4)...C(3) ^{II}	3.75 (1)	C(10)...C(19) ^{III}	3.85 (2)
O(1)...C(9) ^{VI}	3.43 (2)	C(10)...C(15) ^{VIII}	3.95 (1)
O(3)...C(18) ^I	3.40 (1)	C(11)...C(18) ^I	3.60 (2)
C(1)...C(9) ^{VI}	3.53 (2)	C(12)...C(18) ^I	3.74 (1)
C(1)...C(15) ^{VII}	3.69 (1)	C(12)...C(4) ^{II}	3.93 (1)
C(2)...C(15) ^{VII}	3.86 (1)	C(14)...C(16) ^{II}	3.90 (3)
C(5)...C(15) ^{IV}	3.63 (2)	C(14)...C(17) ^{III}	3.84 (2)
C(8)...C'(9) ^V	3.75 (2)		

Symmetry code

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

that of N, indicating that the thermal motion of the C atoms consists mainly of rotational vibrations about the central atom. For this reason their H atoms could not be located.

Fig. 3 is a clinographic projection of the structure showing the molecular packing of TMAIXN in the unit cell. The roughly planar IXN anions form layers, approximately parallel to (104), being interconnected by the tetramethylammonium cations, which are distributed both in and between the layers. Moreover, van der Waals anion-anion interactions are observed. In Table 7 some of the more interesting intermolecular distances shorter than 4.0 Å are given.

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References

- CHATT, J., DUNCANSON, L. A. & VENANZI, L. M. (1956). *Nature (London)*, **177**, 1042-1043.
- D'ADDARIO, A. (1970). PhD thesis, Univ. Microfilms, Ann Arbor, Michigan.
- FRANZINI, M. (1963). *Z. Kristallogr.* **118**, 393-403.
- HATZIKOSTAS, C. C. & MANOUSSAKIS, G. E. (1977). Private communication, Univ. of Thessaloniki, Greece.
- HOSKINS, B. F. & KELLY, B. P. (1970). *J. Chem. Soc. D*, pp. 45-46.
- HOSKINS, B. F. & PANNAN, C. D. (1975). *J. Chem. Soc. Chem. Commun.* pp. 408-409.
- International Tables for X-ray Crystallography* (1968). Vol. III, pp. 275-276. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71-151. Birmingham: Kynoch Press.
- MAIN, P. (1970). Private communication. Univ. of York, England.
- MAIN, P., WOOLFSON, M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN, A System of Computer Programs for the Automatic Solution of Crystal Structures*. Univs. of York, England, and Louvain-la-Neuve, Belgium.
- MERLINO, S. (1969). *Acta Cryst.* **B25**, 2270-2276.
- MERLINO, S. & SARTORI, F. (1971). *Acta Cryst.* **B28**, 972-976.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.
- PEYRONEL, G. & PIGNEDOLI, A. (1967). *Acta Cryst.* **23**, 398-409.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system - version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1978). **B34**, 2146-2150

The Crystal and Molecular Structures of 2,3-Dihydrobenzimidazole-2-spirocyclohexane (at 193 K) and of the (1:1) Complex of 2,3-Dihydrobenzimidazole-2-spirocyclohexane with 5,6-(N,N'-Dipiperidino)isobenzimidazole-2-spirocyclohexane

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The structures of the title compounds have been refined to $R = 0.049$ and 0.082 respectively. 2,3-Dihydrobenzimidazole-2-spirocyclohexane is orthorhombic, with $a = 24.073$ (8), $b = 20.363$ (6), $c = 8.520$ (8) Å, $Z = 16$, space group $Fdd2$. The complex is monoclinic, with $a = 19.98$ (3), $b = 8.72$ (3), $c = 21.40$ (4) Å, $\beta = 122.38^\circ$, $Z = 4$, space group $P2_1/c$. In both structures the dihydrobenzimidazole molecules are linked into chains by hydrogen bonds. The isobenzimidazole molecules in the complex are hydrogen-bonded to this chain at right angles, precluding electronic interaction between the molecules.