Structural Studies of Metal Dithiocarbamates. Part VI.† The Crystal and Molecular Structure of Tetrakis(*NN*-diethyldithiocarbamato)titanium(IV)

By **M. Colapietro** and **A. Vaciago,*** Laboratorio di Strutturistica Chimica 'Giordano Giacomello', C.N.R., Città Universitaria, 00100 Roma, Italy
D. C. Bradley, M. B. Hursthouse,* and **I. F. Rendall,** Department of Chemistry, Queen Mary College, Mile End Road, London E.1

The crystal and molecular structure of the title compound has been determined from data measured on a manual diffractometer. Crystals are triclinic, space-group $P\bar{1}$, with a = 11·435, b = 18·408, c = 15·382 Å, α = 96·39, β = 91·62, γ = 95·08°, and Z = 4. The structure has been refined by least-squares, with anisotropic temperature factors to a final R of 0·097. In each molecule the titanium atom is eight-co-ordinated by the sulphur atoms from four chelating dithiocarbamate ligands. The co-ordination geometry approximates very closely to dodecahedral, with chelation along the *m* edges, giving the D_{2d} isomer. The two symmetry-unrelated molecules in the unit cell are identical, within the limits of experimental error, except for minor conformational differences which can be attributed to packing forces.

There has been considerable interest recently, both in complexes with co-ordination numbers greater than six,[1] particularly eight-co-ordinated,[2,3] and in complexes with dithiocarbamate ligands.[4-9] Recently the structures of the tetrakis(*NN*-diethyldithiocarbamato)- (dtc) complexes Th(dtc)$_4$ [7,9] and NEt$_4$[Np(dtc)$_4$] [8,9] have been determined and the actinide ions shown to be eight-co-ordinate. Although the i.r. and n.m.r. spectra for Ti(dtc)$_4$ and the e.s.r. spectrum for V(dtc)$_4$ were compatible with these also being eight-co-ordinate structures,[10] the small size of the vanadium and titanium atoms still made this uncertain. We have therefore determined the structure of the titanium complex Ti(S$_2$CNEt$_2$)$_4$ in order to establish the eight-co-ordination (so far, we have been unable to obtain suitable crystals of the vanadium compound). Preliminary details of this analysis have already been reported.[11]

EXPERIMENTAL

The compound was prepared according to the method of ref. 10*a* and red plate-like crystals were obtained from benzene–cyclohexane. The single crystals used were sealed in Lindemann capillaries under nitrogen.

Crystal Data.—$C_{20}H_{40}N_4S_8Ti$, M = 641·0, Triclinic, a = 11·435(6),‡ b = 18·408(12), c = 15·382(8) Å, α = 96·39(8), β = 91·62(8), γ = 95·08(9)°, U = 3168 Å^3, D_m = 1·33, Z = 4, D_c = 1·34, $F(000)$ = 1352. Space-group $P\bar{1}$. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 71·8 cm^{-1}.

Cell dimensions were determined by a least-squares fit to the 2θ values for twelve high-angle ($60° < 2\theta < 80°$) reflections. Intensities were measured with a General Electric XRD-6 manual diffractometer by use of Cu-K_α radiation and the stationary-crystal–stationary-counter technique, with a counting time of 10 s. Backgrounds were estimated by calibration with those measured for *ca.* 200 reflections over the range of 2θ used. Three standard reflections were checked regularly during collection, and these showed no significant changes.

The crystal used for data collection had dimensions *ca.* 0·05 × 0·025 × 0·01 cm and was mounted about the *a* axis. 4981 independent reflections in the range $5° < 2\theta < 86°$ were measured, of which 3637 had intensities considered significant [$I > 2{\cdot}5\sigma(I)$] where $\sigma(I)$ is given by $[I + 2 \times \text{background} + (0{\cdot}03I)^2]^{\frac{1}{2}}$. Absorption and extinction corrections were not applied.

Structure Analysis.—The structure was solved by means of Patterson and electron-density syntheses. The positions of the two independent titanium atoms were obtained by comparison of an ordinary Patterson map (F_o^2 values as coefficients) and one computed from coefficients sharpened to 'point-atoms-at-rest'. This was done on the assumption that the thermal vibrations of the sulphur atoms might be slightly larger than those of the titanium atoms, and the changes in peak-heights for Ti ··· Ti, Ti ··· S, and S ··· S vectors would be different. This was in fact the case, although the differences were rather small. The co-ordinates of the titanium atoms were used for a structure-factor calculation and electron-density syntheses. For the former, R was 0·63 and from the latter it was possible to

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† Part V, C. Fabiani, R. Spagna, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1971, **B27**, 1499.

‡ Estimated standard deviations are given in parentheses throughout this paper.

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[4] S. Merlino, *Acta Cryst.*, 1968, **B24**, 1441 and references therein.

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[8] D. Brown, D. G. Holah, and C. E. F. Rickard, *J. Chem. Soc.* (*A*), 1970, 786.

[9] D. Brown, D. G. Holah, and C. E. F. Rickard, AERE Report, AERE R6907, 1971.

[10] (*a*) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 1152; (*b*) D. C. Bradley, R. H. Moss, and K. D. Sales, *Chem. Comm.*, 1969, 1255.

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TABLE 1

Final positional parameters ($\times 10^4$)

	x	y	z
Ti(1)	4206(4)	3113(2)	7204(2)
Ti(2)	966(4)	8016(2)	8122(3)
S(1)	3415(7)	1901(4)	6392(6)
S(2)	1962(5)	3039(3)	6786(4)
S(3)	3491(6)	2898(4)	8693(4)
S(4)	5363(6)	2179(4)	7948(4)
S(5)	5787(6)	4036(3)	7953(4)
S(6)	3386(5)	4350(3)	7764(4)
S(7)	4346(6)	3814(4)	5892(4)
S(8)	5989(6)	2790(3)	6248(4)
S(9)	1400(6)	6701(3)	7673(4)
S(10)	−636(6)	7294(3)	7038(4)
S(11)	−457(5)	7519(3)	9161(4)
S(12)	1991(5)	7755(3)	9574(4)
S(13)	1365(6)	9317(4)	8854(4)
S(14)	−753(6)	8803(3)	7892(4)
S(15)	1596(6)	8488(4)	6700(4)
S(16)	3241(6)	8197(4)	8008(4)
N(1)	1259(20)	1854(15)	5692(16)
N(2)	4413(19)	1767(11)	9394(12)
N(3)	5001(17)	5320(10)	8548(11)
N(4)	6159(16)	3550(10)	4835(11)
N(5)	−331(18)	5877(9)	6756(11)
N(6)	500(17)	6981(11)	10,550(12)
N(7)	−288(20)	10,199(11)	8592(14)
N(8)	3963(20)	8752(12)	6577(15)
C(1)	2057(18)	2263(12)	6245(16)
C(2) [a]	1572	1019	5521
C(3) [a]	1458	1019	4688
C(4)	109(23)	2182(16)	5556(18)
C(5)	−922(30)	1653(22)	5894(21)
C(6)	4436(21)	2236(12)	8750(14)
C(7)	3377(32)	1769(22)	10,075(20)
C(8)	3728(36)	1977(31)	10,909(23)
C(9)	5222(24)	1200(12)	9409(16)
C(10)	4562(32)	454(18)	8901(23)
C(11)	4740(21)	4658(10)	8148(13)
C(12)	6227(23)	5586(15)	8950(17)
C(13)	6980(27)	6026(17)	8313(19)
C(14)	4124(24)	5888(13)	8632(15)
C(15)	3528(32)	5884(20)	9512(19)
C(16)	5544(19)	3407(12)	5544(14)
C(17)	5831(26)	4184(14)	4334(18)
C(18)	4956(28)	3939(18)	3613(17)
C(19)	7129(21)	3130(14)	4550(15)
C(20)	8262(25)	3564(17)	4921(19)
C(21)	98(22)	6537(12)	7116(13)
C(22)	330(27)	5211(12)	6824(16)
C(23)	−119(33)	4813(17)	7614(20)
C(24)	−1541(22)	5741(14)	6285(15)
C(25)	−1443(25)	5821(16)	5329(16)
C(26)	661(20)	7365(11)	9861(15)
C(27)	−673(21)	6604(15)	10,704(16)
C(28)	−859(27)	5850(15)	10,248(18)
C(29)	1526(21)	6814(16)	11,141(15)
C(30)	1453(24)	7263(16)	12,037(15)
C(31)	24(22)	9544(12)	8460(15)
C(32)	455(28)	10,847(12)	8987(19)
C(33)	1226(33)	11,200(16)	8290(21)
C(34)	−1398(46)	10,417(19)	8021(33)
C(35)	−2125(43)	10,304(28)	8605(26)
C(36)	3013(22)	8528(14)	7029(16)
C(37)	3702(29)	8967(19)	5626(20)
C(38)	3775(42)	9837(23)	5868(28)
C(39)	5222(26)	8825(18)	6934(20)
C(40)	5742(36)	8148(28)	6719(31)

[a] Co-ordinates for these atoms not determined uniquely from least-squares refinement. See text.

find 11 of the 16 sulphur atoms. Successive calculations of this type eventually gave the positions of all other atoms except hydrogen. At this point, R was 0·31. Refinement by block-diagonal least-squares with isotropic temperature factors converged to R 0·138 (after repositioning two carbon atoms). Anisotropic refinement of all atoms further reduced R to a final value of 0·097. The weighting scheme used was $w = (6{\cdot}5 + |F_o| + 0{\cdot}004|F_o|^2)^{-1}$. There appears to be some disorder of atoms C(2) and C(3) and the final co-ordinates given for these are computed by combining the results from the refinement and a final difference Fourier synthesis based on structure-factors from which the contribution of these two atoms had been omitted. Apart from these atoms, all shifts, at the end of refinement were $<0{\cdot}6\sigma$. The final atomic positional parameters are given in Table 1. The thermal parameters and $|F_o|$ and F_c values are listed in Supplementary Publication No. SUP 20281 (13 pp., 1 microfiche).* Calculations were carried out on the University of London Atlas computer, by use of the 'X-ray '63' system of programs, compiled by J. M. Stewart and D. High and modified for Atlas by J. Baldwin, and on the UNIVAC 1108 computer of the University of Rome, using the system of programs of the Laboratorio di Strutturistica Chimica.[12] Scattering factors (neutral atoms) for the listed final structure-factors were taken from ref. 13.

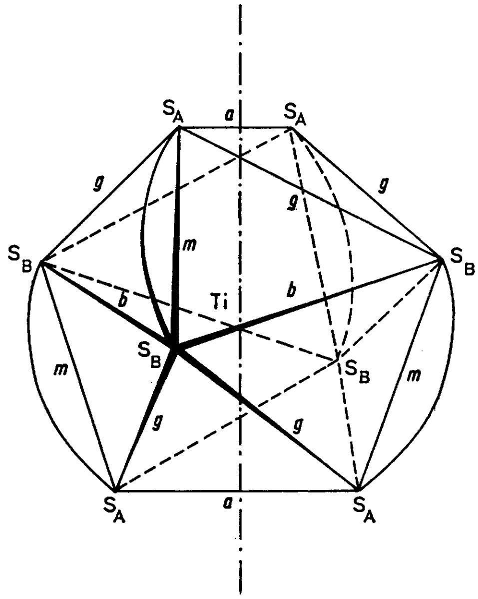

FIGURE 1 Vertex and edge nomenclature for TiS_8 dodecahedron

RESULTS AND DISCUSSION

The asymmetric unit contains two independent $Ti(dtc)_4$ molecules, in each of which the titanium atom is bonded to eight sulphur atoms from four chelating (dtc) ligands. The overall structures of the two molecules are very similar and the co-ordination geometry approximates very closely to dodecahedral. Chelation is along the m edges (Hoard and Silverton notation [2]), which corresponds to the D_{2d} isomer. Figure 1 shows the general molecular configuration, and also the edge and vertex nomenclature. Figure 2, which represents views

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* See note about Supplementary Publications in Notice to Authors No. 7, *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full-size copies).

[12] A. Domenicano, R. Spagna, and A. Vaciago, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1969, **47**, 331.

[13] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

of the two independent molecules as seen down the pseudo $\bar{4}$ axes, shows both the similarity between the two and the closeness of the molecular geometries to the

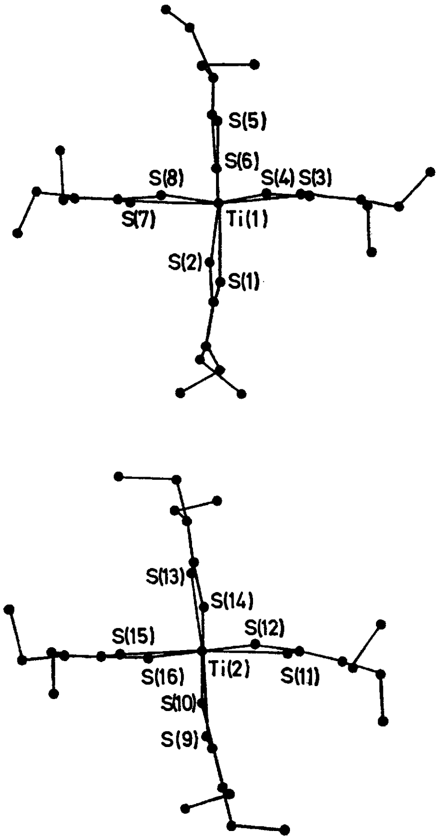

FIGURE 2 Diagram showing view down the pseudo $\bar{4}$ axes of the two independent Ti(dtc)$_4$ molecules

D_{2d} configuration. Figure 3 shows the arrangement of the ligands [labelled (I)—(VIII)] in each molecule, and the atom labelling.

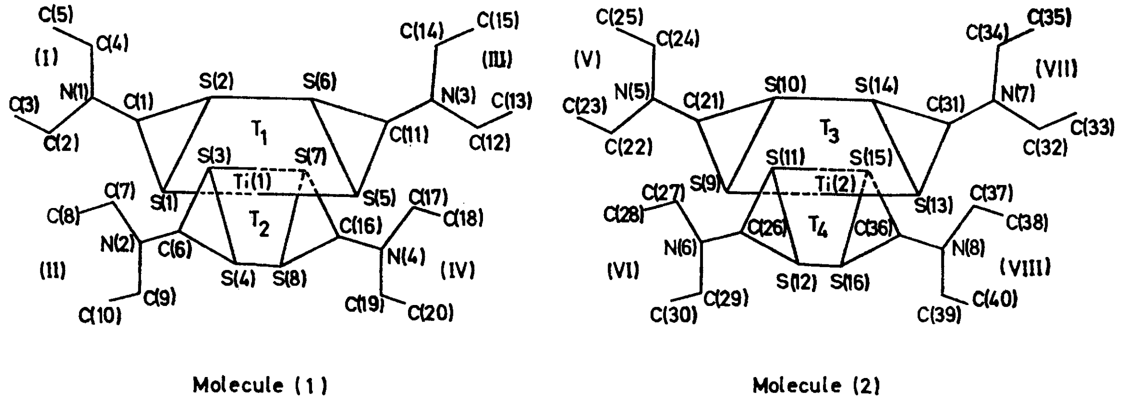

FIGURE 3 Arrangement of ligands and atom labelling in the two Ti(dtc)$_4$ molecules

Co-ordination Geometry.—Interatomic distances and interbond angles relevant to the discussion of the co-ordination geometry are given in Table 2. These show the equivalence between the two molecules. In view of this, the various parameters[2] used to describe the 'shape' of the dodecahedron have been determined by averaging over both molecules. They are as follows: Ti–S_A 2·606(8) Å, Ti–S_B 2·522(8), Ti–S_A/Ti–S_B 1·03, θ_A 35·1(6)°, θ_B 77·5(8)°, a 3·00(6) Å, b 3·64(2) Å, g 3·30(6) Å, and m 2·84(3) Å. Estimated standard deviations (e.s.d.'s) given here and in Figure 4, have been computed from the spread of values in the two molecules for each parameter, by use of the standard formula, $\text{e.s.d.} = \left\{\sum_{i=1}^{n} (x_i - \bar{x})^2/(n-1)\right\}^{\frac{1}{2}}$, where n = No. of values of x_i and $\bar{x}$ is the mean. These values are preferred to those calculated from the individual least-squares since the latter, obtained from the block-diagonal approximation, are likely to be underestimated.

A dodecahedron may be described as being formed from two mutually orthogonal interlocking trapezoids (see Figure 3). The least-squares best planes defined by each trapezoid and the metal atom in the two TiS_8 dodecahedra are given in Table 3. The dihedral angles between related planes are 89·8° [T_1/T_2, molecule Ti(1)] and 87·8° [T_3/T_4, Ti(2)], both values being very close to the 90° required for D_{2d} symmetry. The deviations of the atoms from their respective planes are similar to values found in other structures,[7,8] and probably arise from steric forces.

All calculations described serve to show the close approximations to D_{2d} geometry in both co-ordination polyhedra. They also show how closely the geometry approximates to the ideal model described by Hoard and Silverton[2] and to the requirements for d^4sp^3 hybridisation.[14]

Perhaps the most interesting aspect of this result is the acceptance, in the formation of the molecules, of some extremely short interligand non-bonding contacts. Thus the two a edges in each molecule are only *ca.* 3·0 Å and the g edges are, on average, 3·3 Å. These values are much shorter than the van der Waals diameter of the sulphur atom, 3·7 Å. This situation is not unique however, since equally tight 'co-ordination packing' occurs in the seven-co-ordinate molybdenum complex

[14] G. Racah, *J. Chem. Phys.*, 1943, **11**, 214.

$Mo(NO)(S_2CNBu^n{}_2)_3$,[5g] where there are S · · · S non-bonding contacts of 2·95—3·08 Å. Similarly, the *a* edges in the dodecahedral $Ti(NO_3)_4$ structure[15] are 2·51 Å, compared with a normal van der Waals O · · · O contact of 2·8 Å.

It is possible that the rather severe steric repulsions in the co-ordination sphere are causing a lengthening of the Ti–S_A bonds. The eight-co-ordinate covalent radius for Ti is clearly a difficult parameter to define. In the complex $TiCl_4(diars)_2$[16] [diars = *o*-phenylenebis(dimethylarsine)] the values obtained by subtracting the covalent radius of the ligand atoms from the bond lengths are 1·50 Å (Ti–As bonds) and 1·47 Å (Ti–Cl bonds). From the complex $Ti(NO_3)_4$,[15] a value of 1·41 Å is found. The values for the A and B bonds in $Ti(dtc)_4$ are 1·566 and 1·482 Å respectively. The latter value would therefore seem to be equal to that expected for a normal single bond, whilst the value for the A bonds indicates some lengthening. Indeed, Hoard *et al.*[2,17] have suggested that a lengthening of this type was to be expected owing to the difference in energy (*ca.* 8 kcal. mol^{-1} in a ZrO_8 species) between A · · · A and B · · · B repulsions.

TABLE 2

Interatomic distances in the TiS_8 dodecahedra. Estimated standard deviations are those obtained from the block-diagonal least-squares refinement

Ligand parameter	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
Ti–S_A	2·616(7)	2·603(8)	2·605(7)	2·619(7)	2·609(7)	2·605(7)	2·582(8)	2·606(8)
Ti–S_B	2·513(8)	2·514(7)	2·526(7)	2·514(8)	2·537(7)	2·501(7)	2·527(7)	2·541(8)
Bite (*m* edge)	2·811(8)	2·820(8)	2·868(8)	2·860(8)	2·850(7)	2·837(7)	2·834(8)	2·842(9)
Angle of bite	66·4(3)	66·9(2)	67·9(2)	67·8(2)	67·2(2)	67·5(2)	67·4(2)	67·0(2)
θ_A	35·3(1)	35·6(1)	35·3(1)	35·6(1)	34·7(1)	35·0(1)	34·7(1)	35·0(1)
θ_B	77·5(2)	76·6(1)	77·5(2)	76·6(1)	78·2(1)	77·9(1)	78·2(1)	77·9(1)
a edges	S(2)—S(6) 3·016(8)		S(4)—S(8) 3·038(9)		S(10)—S(14) 2·989(9)		S(12)—S(16) 2·953(8)	
b edges	S(1)—S(3) 3·79(1)	S(1)—S(7) 3·76(1)	S(3)—S(5) 3·51(1)	S(5)—S(7) 3·50(1)	S(9)—S(11) 3·48(1)	S(9)—S(15) 3·75(1)	S(11)—S(13) 3·83(1)	S(13)—S(15) 3·52(9)
g edges	S(1)—S(4) 3·19(1)	S(1)—S(8) 3·26(1)	S(2)—S(3) 3·42(1)	S(2)—S(7) 3·37(1)	S(3)—S(6) 3·18(1)	S(4)—S(5) 3·41(1)	S(5)—S(8) 3·31(1)	S(6)—S(7) 3·20(1)
	S(9)—S(12) 3·34(1)	S(9)—S(16) 3·30(1)	S(10)—S(11) 3·25(1)	S(10)—S(15) 3·31(1)	S(11)—S(14) 3·26(1)	S(12)—S(13) 3·32(1)	S(13)—S(16) 3·30(1)	S(14)—S(15) 3·35(1)

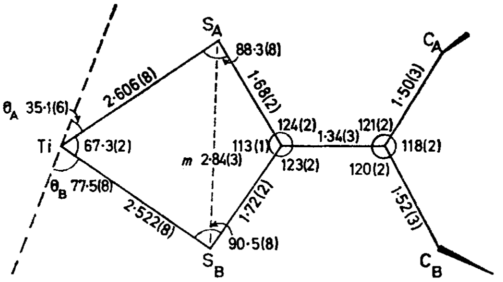

FIGURE 4 Dimensions of the 'average ligand'. Estimated standard deviations calculated from spread of individual values for each parameter

There is an alternative explanation for the Ti–S_A/Ti–S_B difference which would also involve bond-lengthening due to steric interactions, but this would be countered, in some of the bonds, by shortening as a result of π bonding. In relative terms, the *a* edges in $Ti(dtc)_4$ are much shorter than those[18] in $[ZrOx_4]^{4-}$ whilst the *g* edges in the Ti complex represent the same % shortening (from the normal van der Waals distance) as the *a* edges in the $ZrOx_4$ anion. Thus we might argue that the effect of the repulsions in the co-ordination sphere would be to lengthen all bonds. Then the shortening of the Ti–S_B bonds might be due to π bonding. Group theoretical arguments show that the only metal *s*, *p*, or *d* orbital having the correct symmetry for π bonding is

TABLE 3

Results of least-squares plane calculation in the dodecahedral trapezoids. The equations of the planes, calculated using fractional co-ordinates for the atoms, are given in direct space, *i.e.* referred to the unit-cell axes. The deviations (Å) of the atoms from the planes are given in square brackets

Plane T_1:
Ti(1), S(1), S(2), S(5), S(6) $-2{\cdot}25x - 7{\cdot}93y + 14{\cdot}18z = 6{\cdot}78$
[Ti(1) −0·012, S(1) −0·003, S(2) 0·014, S(5) 0·013, S(6) −0·011]

Plane T_2:
Ti(1), S(3), S(4), S(7), S(8) $6{\cdot}25x + 11{\cdot}66y + 5{\cdot}93z = 10{\cdot}64$
[Ti(1) 0·111, S(3) −0·074, S(4) 0·036, S(7) −0·015, S(8) 0·059]

Plane T_3:
Ti(2), S(9), S(10), S(13), S(14) $-5{\cdot}19x - 6{\cdot}45y + 13{\cdot}10z = 4{\cdot}95$
[Ti(2) −0·018, S(9) 0·053, S(10) 0·104, S(13) 0·069, S(14) −0·101]

Plane T_4:
Ti(2), S(11), S(12), S(15), S(16) $-1{\cdot}70x + 16{\cdot}77y + 4{\cdot}69z = 17{\cdot}05$
[Ti(2) −0·031, S(11) 0·074, S(12) −0·099, S(15) −0·050, S(16) 0·105]

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[15] C. D. Garner and S. C. Wallwork, *J. Chem. Soc.* (*A*), 1966, 1496.

[16] R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *Nature*, 1961, **192**, 222.

[17] J. L. Hoard, E. W. Silverton, and J. V. Silverton, *J. Amer. Chem. Soc.*, 1968, **90**, 2300.

[18] G. L. Glen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1963, **2**, 250.

$d_{x^2-y^2}$ (B_1). This could interact with filled ligand orbitals of B_1 symmetry (Figure 5). Clearly, the S atoms in the B sites are in a much better position to effect overlap of this type and are therefore more likely to be involved in π bonding than the atoms at the A sites.

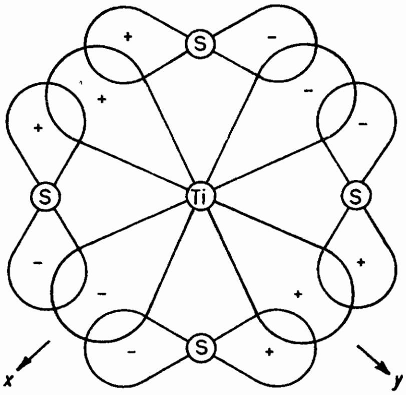

FIGURE 5 Diagram to show possible mode of π bonding between the $d_{x^2-y^2}$ orbital of the titanium atoms and ligand orbitals of B_1 symmetry (projection on to xy plane)

Without any further evidence, it is difficult to decide which of the two effects is more effective in causing the difference in Ti–S bond lengths. It is possible, however, that selective π bonding might also influence the geometry of the ligand, particularly the S–C bond lengths. This will be considered in the next section.

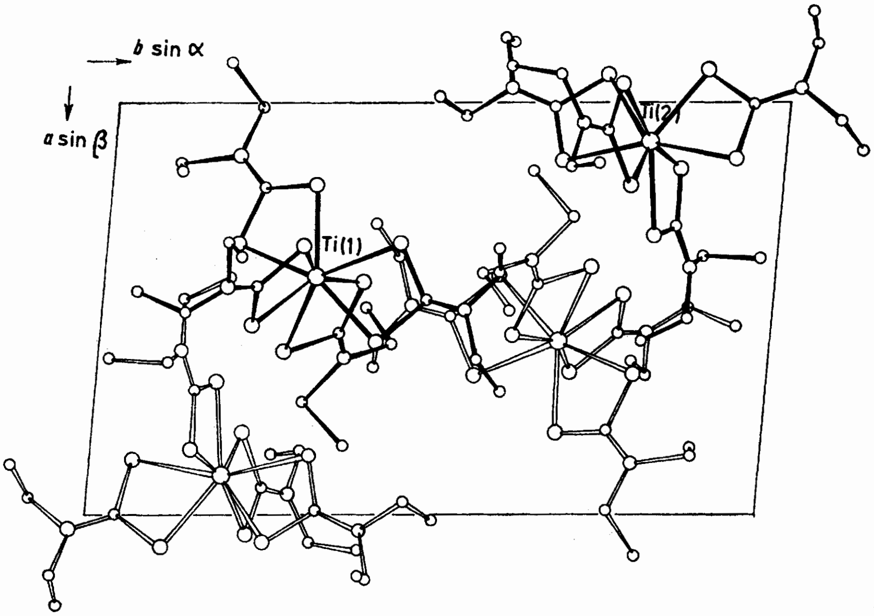

FIGURE 6 Diagram of unit cell; projection down c

Ligand Geometry.—Full details of the interatomic distances and bond angles in the eight ligands (I)—(VIII) are listed in Supplementary Publication No. 20281 (see earlier). Dimensions for an ' average ' ligand are shown in Figure 4, where the errors given are estimated standard deviations derived from the spread of values.

Figure 4 shows that there is no significant difference between S_A–C and S_B–C bond lengths. This in itself does not preclude the possibility of the S_B atoms being involved in π bonding since the difference in S–C bond lengths, which might occur, will probably be smaller than the corresponding Ti–S differences and thus be masked, unfortunately, by the general inaccuracy of the parameters. One result which is not masked is the shortness of the S–C and C–N bonds, implying delocalised multiple bonding over the S_2CN system which is quite normal for dithiocarbamates.

It has been said [4] that in general the dimensions of the dithiocarbamate ligand are remarkably constant irrespective of the oxidation state and co-ordination number of the atom to which it is bonded. Exceptions to this rule do occur, and in these cases [6] there is always a considerable difference in metal–sulphur bond lengths.

The participation, by the nitrogen atom of the dtc ligands, in delocalisation, results in a good degree of planarity over the major portion of the ligand (from sulphur atoms to α-carbon atoms of the alkyl groups). The results of mean-plane calculations of this part of the ligands are also included in the Supplementary Publication.

The directions of these planes may be compared with those for the dodecahedral trapezoids, since for perfect D_{2d} symmetry, these should be the same. In terms of the labelling of Figure 3, the dihedral angles between relevant planes are given in Table 4. The deviation from

TABLE 4

Ligand	Angle (°)	Trapezoid	Angle (°)	Ligand
(I)	10·2	T_1	2·0	(III)
(II)	8·6	T_2	5·6	(IV)
(V)	8·7	T_3	8·0	(VII)
(VI)	14·7	T_4	1·4	(VIII)

zero of some of these values indicates a slight folding about the S · · · S lines by the ligands concerned. There are no really short interligand intramolecular contacts which could account for these distortions. On the other hand, there are a number of intermolecular contacts shorter than the sum of the van der Waals radii. The shortest of these, between atom S(3) (at x, y, z) and atom C(27) (at $\bar{x}, \bar{y} + 1, \bar{z} + 2$) is 3·55 Å and is almost certainly the cause of the folding of ligand (VI).

Molecular Packing.—The shortest intermolecular contact is 3·55 Å; there are several <4 Å, but these involve β-carbon atoms of the ethyl groups, which might be considered to have a considerable degree of rotational freedom. They are therefore not likely to exert any significant distortive forces. The overall picture is therefore one of a rather loosely packed structure. This is in agreement with the fairly low-angle cut-off (*ca.* 90° in 2θ) of the *X*-ray data. A diagram showing the molecular packing is given in Figure 6.

There is considerable difference between the crystal structures adopted by $Ti(dtc)_4$ and $Th(dtc)_4$.[7] The latter compound crystallises in space-group *C*2/*c* and although the unit-cell edges of the two are rather similar, the symmetries are quite different. It does not seem possible to redefine either unit cell to get closer similarities. The only real differences between the molecules are in the metal–sulphur bond lengths, and it is difficult to imagine that these are the cause of the symmetry differences. It would therefore seem likely that these two structures could be considered to be equivalent to the formation of polymorphs by a single compound.

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