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## The Crystal and Molecular Structure of Bis(cyclopentadienyl)( $\sigma$ -allyl)(carbon disulphide)niobium

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(Received 21 July 1976; accepted 23 September 1976)

Crystals of the title compound are orthorhombic, space group  $P2_12_12_1$ ,  $a = 7.59(1)$ ,  $b = 13.60(1)$ ,  $c = 26.47(2)$  Å,  $Z = 8$ . 1178 independent reflexions above background were measured on a diffractometer and the structure has been refined to  $R = 0.070$ . There are two independent monomers in the asymmetric unit related by a pseudo-centre of symmetry which caused considerable difficulty in the refinement. Each Nb atom is bonded to two cyclopentadienyl rings [2.372 (22)–2.500 (21) Å], to an allyl group [2.309 (31) Å] and to carbon disulphide through a S atom [2.518 (9) Å] and a C atom [2.241 (21) Å]. This C–S bond length is 1.720 (24) Å while the other C–S retains much of its double-bond character [1.574 (23) Å]. The S–C–S angle is 136.8 (14)°. The overall geometry of the complex is similar to that usually found for  $(C_5H_5)_2MX_2$  complexes.

We have carried out and report here the structure determination of bis(cyclopentadienyl)( $\sigma$ -allyl)(carbon disulphide)niobium (I), a complex recently prepared by Fowles, Pu & Rice (1973). Only one structure including the carbon disulphide group bonded to a transition metal has previously been reported, namely  $Pt(PPh_3)_2(CS_2)$  (Mason & Rae, 1970). In that structure the metal atom is bonded to one S and the C atom with a S–C–S angle of 136 (4)°. The dihedral angle between the  $CS_2$  and  $PtP_2$  planes is 6°. We were interested to see whether the bonding of the carbon disulphide group to an early transition metal would be equivalent.

The structures of a series of complexes of the form  $(C_5H_5)_2MX_2$  ( $X$ =monodentate ligand) in which the metal atom is bonded to two non-parallel  $\eta^5$ -cyclopentadienyl rings and to two ligands  $X$  in the plane between the rings have been summarized by Prout, Cam-

eron, Forder, Critchley, Denton & Rees (1974). Although (I) has the form  $(C_5H_5)_2MX(X-X)$ ,  $X-X$  being a bidentate ligand, its structure might be expected to be comparable.

### Experimental

Crystals (red-wine plates) were prepared as described previously by Fowles, Pu & Rice (1973).

### Crystal data

$C_{14}H_{15}S_2Nb$ ,  $M_r = 340.31$ , orthorhombic,  $a = 7.59(1)$ ,  $b = 13.60(1)$ ,  $c = 26.47(2)$  Å,  $Z = 8$ ,  $U = 2732.3$  Å<sup>3</sup>,  $D_m = 1.68(2)$ ,  $D_c = 1.66$  g cm<sup>-3</sup>,  $\lambda(MoK\alpha) = 0.7107$  Å,  $\mu = 17.85$  cm<sup>-1</sup>; space group  $P2_12_12_1$

from systematic absences  $h00$   $h = 2n + 1$ ,  $0k0$   $k = 2n + 1$ , and  $00l$   $l = 2n + 1$ .

A crystal of approximate size  $0.5 \times 0.3 \times 0.05$  mm was mounted with the  $a$  axis parallel to the instrument axis of a General Electric XRD-5 apparatus which was used to measure diffraction intensities and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zr-filtered Mo X-radiation was used with a  $4^\circ$  take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflexions whose intensities were seriously affected by the streaking of other orders. For other reflexions, backgrounds were taken from plots of background as a function of  $2\theta$ . Several standard reflexions were measured during the course of the experiment but no crystal decay was observed. Two thousand and fifty independent reflexions were measured with  $2\theta < 45^\circ$  by the stationary-crystal stationary-counter method and 1178 with  $I > s(I)$  were used in subsequent calculations. No absorption or extinction corrections were applied.

### Structure determination

The structure was solved by Patterson and Fourier methods. The two independent molecules in the asymmetric unit were of opposite enantiomorph and coordinates were approximately related by the transformation  $0.48 - x$ ,  $0.26 - y$ ,  $0.50 - z$ . Attempts to refine the parameters of the two molecules independently by the normal least-squares procedure were unsuccessful. As is so often found when there is a high correlation between parameters, the shifts obtained reduced the correlation but the resulting parameters did not make chemical sense. For example, the lengths of the C=C double bond in the allyl group became 1.04, 1.24 Å in the two molecules and C—C bond lengths in the cyclopentadienyl rings ranged from 1.11 to 1.73 Å.\* Accordingly we refined the structure with the *SHELX* system of programs (Sheldrick, 1973) in which provision is made for rigid-body refinement and also for the introduction of constraints on bond lengths.† We refined the four cyclopentadienyl rings as rigid bodies ( $D_{5h}$  geometry, C—C 1.42, C—H 1.08 Å) and the least-squares refinement converged successfully despite the correlation between ring parameters. We then constrained the geometries of the CS<sub>2</sub> group and of the allyl group to be equivalent in the two independent molecules. The lengths C—S, C—S and S···S in the former were equated as were the three bond lengths and Nb···

\* An additional cause for unacceptable values could be disorder in the cyclopentadienyl rings. Observed and difference Fourier maps were studied and there is some residual electron density in the latter, particularly in the area of rings 2A and 2B, that make this a possibility. However, we were not able to find an obvious (or refinable) alternative orientation of any of the four independent rings.

† Use of this technique has been reviewed by Bartell, Romensko & Wong (1975).

C(3) and C(2)···C(4) contacts in the Nb,C(2),C(3), C(4) allyl group. These eight distances were introduced as additional variables in the least-squares refinement;  $R$  dropped to 0.070 and convergence was obtained.

We then freed the constraints on the CS<sub>2</sub> and allyl groups but again parameters converged to unreasonable values despite a lower  $R$  (0.066). There was thus no alternative but to accept the results of the constrained refinement, in which we assume that there were no significant differences in geometry between carbon disulphide and allyl groups in the two independent molecules. We did obtain some slight differences in the relative orientations of the groups around the metal atoms which might be genuine.

Nb and S atoms were refined anisotropically, C atoms isotropically. All H atoms were included in ideal positions with thermal parameters equivalent to those

Table 1. Atomic parameters ( $\times 10^4$ ) with estimated standard deviations in parentheses [isotropic thermal parameters ( $\times 10^3$ ) are also given]

	$x$	$y$	$z$	$U$
Nb(A)	1437 (3)	1251 (1)	1202 (1)	*
S(1A)	5154 (15)	2068 (9)	436 (4)	*
S(2A)	4615 (11)	981 (7)	1437 (3)	*
C(1A)	4108 (27)	1587 (22)	885 (9)	67 (9)
C(2A)	1254 (44)	407 (28)	1957 (10)	112 (14)
C(3A)	-522 (52)	391 (25)	2221 (12)	109 (13)
C(4A)	-1226 (52)	-325 (29)	2315 (17)	113 (14)
C(11A)	-378 (29)	2632 (16)	1006 (8)	91 (12)
C(12A)	-860 (29)	2325 (16)	1499 (8)	91 (12)
C(13A)	580 (29)	2519 (16)	1827 (8)	89 (12)
C(14A)	1953 (29)	2946 (16)	1536 (8)	85 (11)
C(15A)	1360 (29)	3016 (16)	1028 (8)	74 (9)
C(21A)	-186 (32)	812 (19)	455 (11)	95 (12)
C(22A)	-879 (32)	252 (19)	862 (11)	91 (12)
C(23A)	458 (32)	-400 (19)	1030 (11)	99 (12)
C(24A)	1977 (32)	-244 (19)	728 (11)	116 (14)
C(25A)	1579 (32)	505 (19)	372 (11)	105 (13)
Nb(B)	3390 (3)	1377 (1)	3826 (1)	*
S(1B)	-350 (13)	518 (8)	4571 (4)	*
S(2B)	225 (12)	1695 (7)	3598 (3)	*
C(1B)	706 (27)	996 (18)	4122 (8)	48 (8)
C(2B)	3526 (40)	2201 (20)	3064 (9)	65 (9)
C(3B)	5340 (56)	2373 (31)	2839 (16)	163 (20)
C(4B)	5905 (64)	3145 (38)	2789 (24)	183 (22)
C(11B)	4885 (30)	-113 (15)	4008 (8)	72 (9)
C(12B)	5703 (30)	240 (16)	3561 (8)	84 (11)
C(13B)	4436 (30)	213 (16)	3166 (8)	100 (13)
C(14B)	2835 (30)	-155 (16)	3370 (8)	59 (8)
C(15B)	3113 (30)	-356 (16)	3890 (8)	75 (9)
C(21B)	5144 (25)	1725 (14)	4585 (8)	68 (9)
C(22B)	5735 (25)	2328 (14)	4181 (8)	88 (12)
C(23B)	4353 (25)	2991 (14)	4057 (8)	79 (10)
C(24B)	2912 (25)	2797 (14)	4384 (8)	51 (8)
C(25B)	3400 (25)	2015 (14)	4710 (8)	80 (10)

The following lengths were constrained to be equivalent in the two molecules: C(1)—S(2), C(1)—S(1), S(1)—S(2), Nb—C(2), C(2)—C(3), C(3)—C(4), Nb—C(3), C(2)—C(4).

\* Anisotropic thermal parameters are in Table 2.

of the atoms to which they were bonded, but their parameters were not refined. The weighting scheme, chosen so that  $w\Delta^2$  was constant over ranges of  $F_o$  and  $\sin\theta/\lambda$ , was  $\sqrt{w} = 1$  for  $F_o < 22$  and  $\sqrt{w} = 22/F_o$  for  $F_o > 22$ . In the final cycle of refinement, no shift was  $> 0.20\sigma$ . The correct enantiomorph for molecule *A* (and its opposite for *B*) was determined by a test of the *R* value (coordinates  $x, y, z$  gave 0.0703 and  $\bar{x}, \bar{y}, \bar{z}$  0.0705). A final difference Fourier map showed no significant peaks and the zero-weighted reflexions no serious discrepancies. The anisotropic/isotropic thermal factors take the forms  $\exp(-2\pi^2 \sum_i \Sigma_j U_{ij} h_i h_j b_i b_j)$  ( $i, j = 1, 2, 3$  where  $b_i$  is the  $i$ th reciprocal-lattice dimension) and  $\exp(-8\pi^2 \sin^2\theta/\lambda^2)$  respectively. Calculations were made on a CDC 7600 computer at the University of London Computer Centre. Scattering factors for Nb, S, C and H were taken from *International Tables for X-ray Crystallography* (1974) as were the real and imaginary parts of the anomalous dispersion for Nb and S. Final positions are given in Table 1 together with isotropic thermal parameters. Anisotropic thermal parameters are given in Table 2 and molecular dimensions in Table 3.\*

### Discussion

There are two independent molecules of formula  $(C_5H_5)_2Nb(CS_2)(C_3H_5)$  in the asymmetric unit. By the method of refinement we were unable to show whether there were any significant differences between the geometries and thus mean values are discussed here. The metal atom is bonded to two  $\eta^5$ -cyclopentadienyl rings, a carbon disulphide ligand through a S atom and a C atom, and to an allyl group. Fig. 1 shows molecule *A* together with the atomic numbering scheme. The overall geometry of (I) is very similar to that found in  $(C_5H_5)_2Nb(C_2H_4)(C_2H_5)$  (II) (Guggenberger, Meakin & Tebbe, 1974), with the carbon disulphide group replacing ethylene and the  $\sigma$ -allyl group replacing ethyl.

Both (I) and (II) are of the  $(C_5H_5)_2MX(X-X)$  type and have geometries comparable to the standard

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32199 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

$(C_5H_5)_2MX_2$  type discussed by Prout *et al.* (1974) particularly if the  $X-X$  ligand is considered as monodentate through its midpoint. Twenty molecules of the type  $(C_5H_5)_2MX_2$  are discussed by these authors\* in which the angle between the normals to the cyclopentadienyl rings ranges from 126.0 to 148.2°. However, for Nb compounds a much narrower range is found; 130.9, 129.6 in the two independent molecules

\* A more general list, of 21 complexes containing at least two cyclopentadienyl rings, has been given by Guggenberger (1973).

Table 3. *Molecular dimensions: distances (Å) and angles (°)*

	<i>A</i>	<i>B</i>
Nb-S(2)	2.518 (9)	2.514 (9)
Nb-C(1)	2.241 (21)	*
Nb-C(2)	2.309 (31)	*
Nb-C(11)	2.387 (22)	2.372 (22)
Nb-C(12)	2.408 (22)	2.442 (22)
Nb-C(13)	2.477 (21)	2.488 (21)
Nb-C(14)	2.500 (21)	2.444 (21)
Nb-C(15)	2.445 (21)	2.372 (22)
Nb-C(21)	2.406 (28)	2.456 (21)
Nb-C(22)	2.397 (25)	2.391 (19)
Nb-C(23)	2.409 (24)	2.393 (21)
Nb-C(24)	2.424 (27)	2.458 (20)
Nb-C(25)	2.422 (28)	2.495 (21)
C(1)-S(1)	1.574 (23)	*
C(1)-S(2)	1.720 (24)	*
C(2)-C(3)	1.519 (50)	*
C(3)-C(4)	1.142 (32)	*
S(1)-C(1)-S(2)	136.8 (14)	*
Nb-C(2)-C(3)	117.3 (22)	*
C(2)-C(3)-C(4)	121.9 (37)	*
C(1)-Nb-C(2)	118.6 (10)	117.2 (9)
S(2)-Nb-C(2)	76.8 (9)	75.5 (8)
C(1)-Nb-S(2)	41.8 (6)	41.9 (6)
Geometry around the metal atom†		
CG(1)-Nb-CG(2)	133.0	133.3
CG(1)-Nb-CG(3)	108.4	106.4
CG(1)-Nb-C(2)	104.3	100.4
CG(2)-Nb-CG(3)	106.8	108.3
CG(2)-Nb-C(2)	101.5	106.5
CG(3)-Nb-C(2)	96.5	95.0

\* Values in molecule *B* were constrained in the refinement to equal those in molecule *A* (see text).

† CG(1), CG(2) are the centres of gravity of the two cyclopentadienyl rings. CG(3) is the midpoint of the C(1)-S(2) bond.

Table 2. *Anisotropic thermal parameters ( $\times 10^3$ )*

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Nb( <i>A</i> )	35.5 (16)	33.0 (13)	54.4 (21)	-0.2 (13)	0.0 (15)	-0.0 (13)
S(1 <i>A</i> )	68 (7)	138 (9)	97 (8)	42 (7)	25 (7)	-0 (7)
S(2 <i>A</i> )	42 (5)	87 (6)	97 (7)	22 (6)	-14 (5)	-0 (5)
Nb( <i>B</i> )	34.7 (14)	39.3 (14)	51.9 (21)	-4.7 (13)	-11.5 (15)	1.0 (12)
S(1 <i>B</i> )	47 (6)	115 (8)	115 (9)	32 (7)	-12 (6)	4 (6)
S(2 <i>B</i> )	48 (5)	90 (6)	93 (7)	16 (6)	-24 (5)	2 (5)

of  $(C_5H_5)_2NbCl_2$ , 129.7 in  $[(C_5H_5)_2NbCl]_2O^{2+}$  (Prout *et al.*, 1974), 132.4 in (II) and 129.3, 131.6° in (I). Prout *et al.* (1974) considered that the angle was dependent upon the variations in  $M-C$  bond lengths for, as these decrease, the angle increases in order to keep the H atoms away from the rest of the molecule. As the angles and bond lengths are so similar in these Nb complexes, we concur. In (I) there are differences in the Nb-C distances ranging from 2.372 (22) to 2.500 (21) Å. It is not clear because of the difficulties encountered in the refinement whether these are significant, particularly as there seems to be no relation between the deviations and intramolecular contacts. In (II), distances range from 2.374 (9) to 2.430 (9) Å but are considered equivalent within experimental error. Similar values are also found in  $(C_5H_5)_2NbCl_2$ , 2.33 (4)–2.44 (3) Å, and  $[(C_5H_5)_2NbCl]_2O^{2+}$ , 2.35 (2)–2.46 (2) Å, by Prout *et al.* (1974).

For (I), we have defined a horizontal plane containing atoms Nb, C(2) and the midpoint of the centres of gravity of the two cyclopentadienyl rings, and a projection of the molecule upon this plane is shown in Fig. 2. As can be seen the two rings are almost eclipsed and the molecule as a whole has approximate  $C_s$  symmetry. It is thought (Prout *et al.*, 1974) that whether the rings are eclipsed or staggered (or somewhere in be-

tween) is due to packing effects; examples are known [e.g.  $(C_5H_5)_2NbCl_2$ ] where both ideal conformations are found in the same crystal. The equation of the horizontal plane is shown in Table 4 with atomic deviations.

In (I) the metal atom is  $\sigma$ -bonded to an allyl group with a Nb–C(2) bond length of 2.309 (31) Å, which is equivalent to the Nb–C(ethyl) bond length of 2.316 (8) Å in (II). In that latter structure the ethyl group was coplanar with the metal atom in the horizontal plane between the cyclopentadienyl groups. This is not the case for the allyl group [the C(2), C(3), C(4) plane intersecting the horizontal plane at 65.2, 65.0°] presumably because of the possible intramolecular contacts between H(3) and the cyclopentadienyl rings, or of intermolecular contacts. Certainly the shortest intermolecular contacts involve H atoms from allyl groups [1.98 Å H(4,1B)···H(22A), 2.16 Å H(21B)···H(4,2A<sup>ii</sup>)].\*

The carbon disulphide group is bonded to the metal atom *via* C(1), 2.241 (21), and S(2), 2.518 (9) Å. The other S atom is bent away from the metal atom and is

\* H atoms are numbered according to the C atom to which they are bonded.

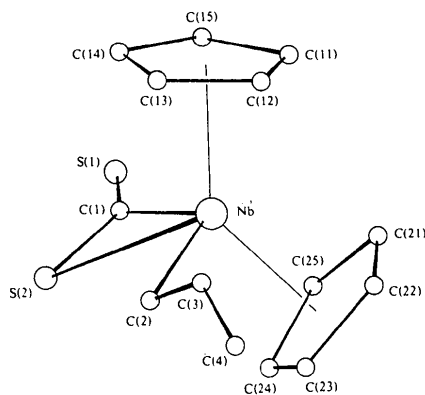


Fig. 1. Atomic numbering scheme.

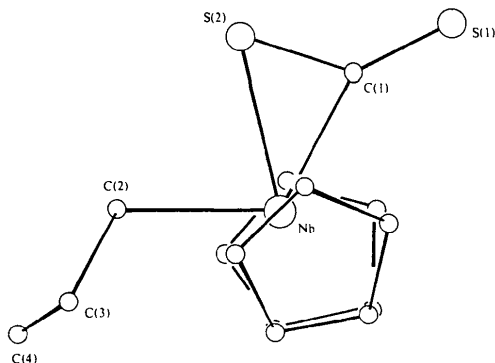


Fig. 2. A view of (I) projected onto the horizontal plane.

Table 4. Least-squares planes in (I) in the form  $Ax + By + Cz = D$ , where  $x, y, z$  are the crystallographic coordinates, with distances (Å) of relevant atoms from the planes

	A	B	C	D
Plane 1: Nb, C(2), midpoint of CG(1)···CG(2)				
in A	−0.03	11.80	13.18	3.05
[S(1)−0.06, S(2)−0.02, C(1)−0.03, C(3) 0.33, C(4)−0.38]				
in B	0.40	11.85	12.89	6.70
[S(1)−0.20, S(2)−0.04, C(1)−0.18, C(3)−0.01, C(4) 0.86]				
Plane 2: Nb, CG(1), CG(2)				
in A	−4.62	−5.18	18.41	0.90
in B	−4.73	−5.54	17.67	4.39
Plane 3: S(1), S(2), C(1)				
in A	0.11	11.86	12.94	3.08
[Nb−0.02, C(2)−0.05, C(3) 0.26, C(4)−0.48]				
in B	0.93	11.33	14.26	7.07
[Nb 0.25, C(2) 0.12, C(3) 0.16, C(4) 1.02]				
Plane 4: C(2), C(3), C(4)				
in A	3.49	−0.32	23.49	5.02
[Nb−1.74, S(2)−0.07]				
in B	3.06	−0.68	24.18	8.34
[Nb 1.86, S(2) 0.31]				
Angles between planes				
in A: 1/2 88.9, 1/3 1.2, 1/4 65.2°				
in B: 1/2 86.4, 1/3 5.4, 1/4 65.0°				

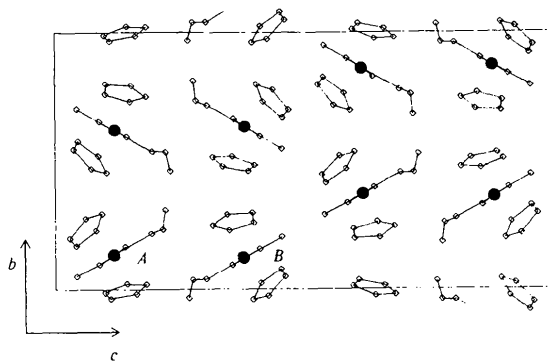


Fig. 3. The unit cell of (I) in the *a* projection.

not bonded to it (3.649 Å). The geometry of this group is identical with that observed in  $\text{Pt}(\text{PPh}_3)_2(\text{CS}_2)$  by Mason & Rae (1970). In that molecule,  $\text{C}(1)\text{--S}(2)$  is 1.72(5),  $\text{C}(2)\text{--S}(1)$  1.54(5) Å and  $\text{S}(1)\text{--C}(1)\text{--S}(2)$   $136.2(44)^\circ$ , compared with 1.720(24), 1.574(23) Å and  $136.8(14)^\circ$  in (I). This similarity also extends to the  $M\text{--C}$  and  $M\text{--S}$  bond lengths which differ by 0.265 Å in this structure and 0.277 Å in (I). In the Pt structure, the  $\text{CS}_2$  moiety is approximately coplanar with the  $\text{PtP}_2$  plane, the dihedral angle between them being  $6^\circ$ . In (I), the angle between the  $\text{CS}_2$  group and the horizontal plane is 1.2,  $5.4^\circ$ . Thus, just like the ethylene group in (II), the carbon disulphide group is close to the horizontal plane. Guggenberger *et al.* (1974) found from models that the ethylene group could fit perpendicular to the plane if the angle between the plane normals were decreased, and decided that the horizontal placement was due at least in part to electronic preference. Certainly in (I), as in (II), the horizontal placement is sterically acceptable as  $\text{S}(1A)\cdots\text{C}(15A)$  and  $\text{C}(25A)$  are similar at 3.52, 3.45 Å,  $\text{S}(2A)\cdots\text{C}(14A)$ ,  $\text{C}(24A)$  at 3.36, 3.21 Å, and any twist of the  $\text{CS}_2$  group would decrease one contact in each pair. Given the very small range in angles between cyclopentadienyl rings in Nb complexes, we consider that the horizontal placement of  $\text{CS}_2$  is inevitable in (I) because of steric effects. However, such a geometry does enhance metal- $\pi^*$  overlap.

In (II), the Nb- $\text{C}$ (ethylene) distances are 2.277(9), 2.320(9) Å, both significantly longer than the Nb- $\text{C}(1)$  bond in (I). The shortest bond is adjacent to the ethyl group [angle  $74.8(3)^\circ$ ] suggesting that the other bond is longer because of steric effects with the cyclopentadienyl rings. In (I) the allyl C atom is adjacent to  $\text{S}(2)$  [ $76.8(8)^\circ$ ]; thus  $\text{S}(1)$  is kept away from the group. The dimensions of the  $\text{--CS}_2$  group show that the  $\text{C}(1)\text{--S}(1)$  bond retains most if not all of its double character, being only slightly longer ( $1\sigma$ ) than the value

Table 5. Intermolecular contacts in (I)  $< 3.70$  Å not involving hydrogen

$\text{C}(14A)\cdots\text{C}(12B^i)$	3.60	$\text{C}(11A)\cdots\text{C}(15B^{ii})$	3.45
$\text{C}(25B)\cdots\text{C}(24A^{iii})$	3.63	$\text{C}(21B)\cdots\text{C}(24B^{iv})$	3.50
$\text{C}(21B)\cdots\text{C}(25B^{iv})$	3.54	$\text{C}(22B)\cdots\text{C}(25B^{iv})$	3.68

Roman numeral superscripts refer to the following equivalent positions relative to the reference set at  $x, y, z$ : (i)  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (ii)  $-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $\frac{1}{2}-x, -y, \frac{1}{2}+z$ ; (iv)  $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$ .

in carbon disulphide (1.554 Å, Guenther, 1959). The  $\text{C}(1)\text{--S}(2)$  bond still retains some double-bond character, its length being significantly less than the single-bond length (1.81 Å). Possibly the C atom in (I) is more strongly bound to Nb than the ethylene C atoms in (II) because of steric interactions between the ethylene H atoms with the remainder of the molecule in that latter complex. The Nb- $\text{S}$  bond lengths are comparable with Nb- $\text{S}$  bonds in other structures, *viz* 2.441 in  $\text{Nb}(\text{S}_2\text{C}_6\text{H}_4)_3^-$  (Bennett, Cowie, Martin & Takats, 1973) and 2.54 Å in  $(\text{C}_2\text{H}_5)_2\text{Nb}(\text{CO})(\text{SH})$  (Kirillova, Gusev, Pasyanskii & Struchkov, 1973).

The packing diagram in the *a* projection is shown in Fig. 3. There are no significant intermolecular contacts less than the sum of the van der Waals radii. Distances less than 3.70 Å are given in Table 5.

We are grateful to A. W. Johans for his assistance with the crystallographic investigations and to G. W. A. Fowles and D. A. Rice for their interest in this work.

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