

## Crystal and Molecular Structure of Trichlorobis-(*N*-methylthioacetamido)niobium(v)

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Crystals of the title compound are monoclinic, space group  $P2_1/c$ , with  $a = 7.39(1)$ ,  $b = 21.78(2)$ ,  $c = 9.40(1)$  Å,  $\beta = 116.6(1)^\circ$ ,  $Z = 4$ . The structure was solved by Patterson and Fourier methods from 1032 independent reflections collected by counter methods, and refined to  $R$  0.066. The seven-co-ordinate monomer is a distorted pentagonal bipyramid: two chlorine atoms in the axial positions [2.359(6), 2.338(6) Å], one chlorine [2.416(5)], two nitrogen [2.231(15), 2.185(13) Å], and two sulphur atoms [2.540(4), 2.526(5) Å] occupying the pentagonal girdle in the sequence Cl, N, S, S, N. There are, therefore, close interactions in the girdle between the chlorine atom and the two *N*-methyl groups (3.17 and 3.18 Å) and these affect the planarity of the girdle. The maximum deviation of a contributing atom from the least-squares plane of the  $ML_5$  unit is 0.15 Å.

In high-co-ordination polyhedra, ligand–ligand repulsions are often found to be the most important factor in the choice of geometry. This is particularly true for complexes containing the larger halogen atoms, chlorine, bromine, and iodine. Thus in seven-co-ordinate complexes containing two or more mutually *cis*-bromine or -iodine atoms, such as  $MoBr_2(dpe)(CO)_3$  [ $dpe = 1,2$ -bis-(diphenylphosphino)ethane],<sup>1</sup> and  $WI_2(dam)(CO)_3$  [ $dam = bis$ (diphenylarsino)methane],<sup>2</sup> it is found that the  $Br \cdots Br$  and  $I \cdots I$  repulsions necessitate  $Br-M-Br$  and  $I-M-I$  angles of *ca.*  $90^\circ$ . This requirement is relaxed for the smaller chlorine atoms and in  $MoCl_2(dpm)_2(CO)_2$  [ $dpm = bis$ (diphenylphosphino)methane]<sup>3</sup> and  $MoCl_2(PMe_2Ph)_3(CO)_2$ ,<sup>4</sup> Cl–M–Cl angles are  $84.4$  and  $86.7^\circ$ .† In a discussion of these structures and others, it has been concluded<sup>5</sup> that halogen atoms occupy the least sterically crowded sites of a particular polyhedron. For example, all known structures of seven-co-ordinate complexes containing two halogen atoms fall into just three categories (*a*) halogen atoms in the axial positions of a pentagonal bipyramid (P.B.), symmetry  $D_{5h}$ , *e.g.*  $MeTaCl_2(MeN_2O_2)_2$ ;<sup>6</sup> (*b*) halogen atoms in the uncapped face of a capped octahedron (C.O.),  $C_{3v}$ , refs. 1 and 2; and (*c*) one halogen atom in the

capping position and one in the capped quadrilateral face of a capped trigonal prism (C.T.P.)  $C_{2v}$ , ref. 3, *e.g.*  $Me_3TaCl_2(2,2'$ -bipyridyl).<sup>5</sup> In addition, attempts have been made to relate the choice of polyhedra between the three ideal types (P.B., C.O., or C.T.P.) with the number of halogen atoms in a particular molecule.<sup>5,7</sup>

There have been very few *X*-ray structure determinations of seven-co-ordinate monomeric complexes containing three or more halogen atoms. Of these examples,  $WOCl_4(diars)$  [ $diars = o$ -phenylenebis(dimethylarsine)]<sup>8</sup> is exceptional as the multiply bonded oxygen atom takes precedence over the chlorine atoms and occupies an axial position of a P.B., while the others  $\{[W(CO)_4Br_3]^-$ ,<sup>9</sup>  $MoBr_4(PMe_2Ph)_3$ ,<sup>10</sup> and  $MoCl_4(PMe_2Ph)_3$ <sup>11</sup> are C.O. with three halogen atoms occupying the uncapped face, where L–M–L angles are *ca.*  $90^\circ$ . This is the only possible geometry for three halogen atoms mutually *cis*, but other geometries which contain either one or no pair of *cis*-halogens were considered to be equally likely for minimisation of ligand–ligand repulsions. Accordingly, we have determined the crystal structure, which we report here, of a molecule which is unsuited to the C.O. geometry on account of the small chelate bites, namely trichlorobis-(*N*-methylthioacetamide)niobium-

† In these examples, the metal–halogen bond lengths are comparable with those found in six-co-ordinate molecules. With M–Cl bond lengthening, the Cl–M–Cl angles can be reduced as in  $WOCl_4(diars)$ ,<sup>8</sup> where angles of  $76^\circ$  are found.

<sup>1</sup> M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329.

<sup>2</sup> M. G. B. Drew and A. P. Wolters, to be published.

<sup>3</sup> M. G. B. Drew, A. P. Wolters, and I. B. Tomkins, to be published.

<sup>4</sup> A. Mawby and G. E. Pringle, *J. Inorg. Nuclear Chem.*, 1972, **34**, 517.

<sup>5</sup> M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 1830.

<sup>6</sup> M. G. B. Drew and J. D. Wilkins, *J. Organometallic Chem.*, in the press.

<sup>7</sup> M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1973, 2664.

<sup>8</sup> M. G. B. Drew and R. Mandyczewsky, *Chem. Comm.*, 1970, 292.

<sup>9</sup> M. G. B. Drew, J. D. Wilkins, and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 1278.

<sup>10</sup> M. G. B. Drew and A. P. Wolters, *J.C.S. Chem. Comm.*, 1972, 457.

<sup>11</sup> L. M. Muir, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 59.

(v),  $\text{NbCl}_3[\text{NMeC}(\text{S})\text{Me}]_2$ , (I). This molecule was prepared during a study of the reactions of isothiocyanates with methylniobium(v) and methyltantalum(v) chlorides.<sup>12</sup> The resulting compounds contain thioacetamide groups arising from insertion of the isothiocyanates into the metal-carbon bonds.

#### EXPERIMENTAL

Crystals were prepared as described previously,<sup>12</sup> and recrystallised from dichloromethane-pentane (4:1, v/v) by slow evaporation.

*Crystal Data.*— $\text{C}_6\text{H}_{12}\text{Cl}_3\text{N}_2\text{S}_2$ ,  $M = 375.6$ ,  $a = 7.39(1)$ ,  $b = 21.78(2)$ ,  $c = 9.40(1)$  Å,  $\beta = 116.6(1)^\circ$ ,  $U = 1353.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.80(5)$ ,  $D_c = 1.84$ ,  $F(000) = 744$ , Mo- $K_\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu(\text{Mo}-K_\alpha) = 15.34$  cm<sup>-1</sup>. Space group  $P2_1/c$  from systematic absences:  $0k0$ ,  $k = 2n + 1$ , and  $h0l$ ,  $l = 2n + 1$ .

A crystal with dimensions *ca.*  $0.2 \times 0.05 \times 0.05$  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. Zirconium-filtered molybdenum X-rays were used. The stationary-crystal-stationary-counter method was used with a  $4^\circ$  take-off angle and a counting time of 10 s. Individual backgrounds were taken for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of  $2\theta$ . Several standard reflections were measured repeatedly during the course of the experiment but no significant change in intensity was detected. 1745 Independent reflections were measured with  $2\theta < 45^\circ$ . The standard deviation of the reflections,  $\sigma(I)$ , was taken to be  $[I + 2E + (0.03I^2)^{1/2}]$ , where  $E$  is the estimated background of the reflection and  $I$  the intensity. 1032 Reflections with  $I > \sigma(I)$  were used in subsequent calculations. This small percentage of significant reflections is due to the small size of the crystal used in the experiment. We were unable to grow bigger ones. No extinction or absorption corrections were applied.

*Structure Determination.*—The positions of the molybdenum atoms were determined from a Patterson function; Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least squares. The weighting scheme, chosen to give average values of  $w\Delta^2$  for groups of reflections independent of the value of  $F_o$  and  $\sin \theta/\lambda$ , was  $\sqrt{w} = 1$  for  $F_o < 55$  and  $\sqrt{w} = 55/F_o$  for  $F_o > 55$ . Calculations were made on CDC 7600 computer at the University of London Computer Centre<sup>13</sup> and with some of our own programs on an ICL 1904S at Reading University. Atomic scattering factors for niobium, chlorine, sulphur, nitrogen, and carbon were taken from ref. 14, together with corrections for the real and imaginary part of the anomalous dispersion for niobium, chlorine, and sulphur. The anisotropic thermal parameter is defined as  $\exp - 2\pi^2 \sum_{i,j} U_{ij} h_i h_j b_j^2$  ( $i, j = 1, 2, \text{ or } 3$ ), where  $b_i$  is the  $i$ th reciprocal lattice dimension. All atoms were refined aniso-

<sup>12</sup> J. D. Wilkins, *J. Organometallic Chem.*, in the press.

<sup>13</sup> 'X-Ray '67' system of programs, ed. J. M. Stewart, University of Maryland Technical Report TR 67 58, 1967, revised July 1970.

<sup>14</sup> 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

TABLE 1

Atomic co-ordinates ( $\times 10^4$ ), with estimated standard deviations in parentheses

Atom	$x$	$y$	$z$
Nb	3102(2)	1201(1)	1803(2)
Cl(1)	0789(7)	0924(2)	2788(5)
Cl(2)	5393(6)	1504(2)	0851(5)
Cl(3)	4853(8)	1796(2)	4205(6)
S(1A)	2754(7)	0134(2)	0654(5)
S(1B)	0139(7)	1206(2)	-0961(5)
N(1A)	5395(20)	0536(7)	3269(16)
N(1B)	1596(22)	2101(7)	0867(18)
C(1A)	4948(27)	0018(9)	2431(23)
C(2A)	7318(28)	0548(10)	4789(25)
C(3A)	6093(32)	-0577(9)	2843(23)
C(1B)	0154(29)	1970(8)	-0485(22)
C(2B)	2136(36)	2742(10)	1547(27)
C(3B)	-1339(29)	2435(9)	-1653(22)

TABLE 2

Anisotropic thermal parameters ( $\times 10^3$ ), with estimated standard deviations in parentheses

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Nb	34.6(9)	29.9(8)	37.6(9)	-1.0(7)	10.8(6)	-0.5(7)
Cl(1)	49(3)	63(3)	56(3)	04(2)	25(2)	13(2)
Cl(2)	46(3)	45(3)	57(3)	-07(2)	25(2)	-05(2)
Cl(3)	64(3)	59(3)	50(3)	-08(3)	16(3)	-13(2)
S(1A)	48(3)	38(3)	45(3)	01(2)	08(2)	-03(2)
S(1B)	49(3)	42(3)	50(3)	00(2)	07(2)	02(2)
N(1A)	49(9)	59(10)	50(10)	-09(8)	08(8)	-18(8)
N(1B)	53(9)	71(11)	55(10)	-02(8)	18(8)	-10(8)
C(1A)	50(11)	60(13)	63(12)	23(10)	29(10)	30(10)
C(2A)	46(11)	79(15)	76(14)	-13(11)	02(11)	-05(12)
C(3A)	95(16)	47(11)	66(13)	38(11)	19(12)	-06(11)
C(1B)	59(11)	48(11)	51(12)	19(09)	21(11)	22(9)
C(2B)	99(17)	51(13)	92(17)	-22(12)	40(14)	-16(12)
C(3B)	65(13)	58(13)	57(12)	22(10)	10(11)	21(10)

TABLE 3

Molecular dimensions

(a) Bond distances (Å)			
Nb-Cl(1)	2.359(6)	Nb-Cl(2)	2.338(6)
Nb-Cl(3)	2.416(5)	Nb-S(1B)	2.540(4)
Nb-S(1A)	2.526(5)	Nb-N(1B)	2.231(15)
Nb-N(1A)	2.185(13)	S(1B)-C(1B)	1.721(19)
S(1A)-C(1A)	1.748(16)	N(1B)-C(1B)	1.273(20)
N(1A)-C(1A)	1.330(25)	C(1B)-C(3B)	1.537(24)
C(1A)-C(3A)	1.502(28)	N(1B)-C(2B)	1.513(26)
N(1A)-C(2A)	1.498(28)		
(b) Bond angles ( $^\circ$ )			
Cl(1)-Nb-Cl(2)	178.3(2)	Cl(1)-Nb-S(1B)	87.6(2)
Cl(1)-Nb-S(1A)	88.8(2)	Cl(1)-Nb-N(1B)	93.3(5)
Cl(1)-Nb-N(1A)	94.4(5)		
Cl(1)-Nb-Cl(3)	87.1(2)	Cl(2)-Nb-S(1B)	92.7(2)
Cl(2)-Nb-S(1A)	92.8(2)	Cl(2)-Nb-N(1B)	85.4(4)
Cl(2)-Nb-N(1A)	86.5(5)		
Cl(2)-Nb-Cl(3)	91.7(2)	S(1B)-Nb-N(1B)	62.8(4)
S(1A)-Nb-N(1A)	64.0(4)	S(1B)-Nb-N(1A)	135.9(4)
S(1A)-Nb-N(1B)	134.6(4)		
S(1A)-Nb-S(1B)	72.0(2)		
N(1A)-Nb-N(1B)	160.0(5)	Cl(3)-Nb-S(1B)	144.0(2)
Cl(3)-Nb-S(1A)	143.4(2)	Cl(3)-Nb-N(1B)	82.0(4)
Cl(3)-Nb-N(1A)	80.0(4)	Nb-N(1B)-C(1B)	104.1(12)
Nb-N(1A)-C(2A)	105.7(9)	Nb-N(1B)-C(2B)	130.8(10)
Nb-N(1A)-C(1A)	136.6(13)	C(1B)-N(1B)-C(2B)	125.0(15)
C(1A)-N(1A)-C(2A)	117.3(15)	Nb-S(1B)-C(1B)	80.6(6)
Nb-S(1A)-C(1A)	81.4(7)	N(1B)-C(1B)-S(1B)	112.4(13)
N(1A)-C(1A)-S(1A)	108.8(13)	N(1B)-C(1B)-C(3B)	125.3(17)
N(1A)-C(1A)-C(3A)	128.1(14)	S(1B)-C(1B)-C(3B)	122.1(12)
S(1A)-C(1A)-C(3A)	123.1(14)		

tropically to  $R$  0.066 for the 1032 observed reflections. In the final cycle, no shift was  $> 0.05\sigma$ . In a final difference-Fourier map, no significant peaks were observed. Hydrogen-atom positions of the methyl groups were not

obvious and therefore not included in the refinement. The 713 reflections given zero weight in the refinement showed no large discrepancies. The final list of positional coordinates and thermal parameters, together with standard deviations are given in Tables 1 and 2. Molecular dimensions are given in Table 3. Observed and calculated structure factors are listed in Supplementary Publication SUP 20870 (5 pp.).\*

#### DISCUSSION

The molecule (I) is shown in Figure 1 with the atomic numbering scheme. Both the *N*-methylthioacetamide

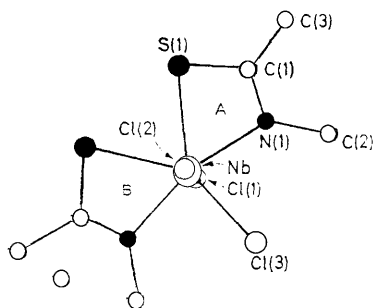


FIGURE 1 The molecule

ligands are bidentate, as predicted,<sup>12</sup> bonding to the metal atom *via* a nitrogen and a sulphur atom. The niobium atom is seven-co-ordinate being bonded to two such bidentate ligands and three chlorine atoms. The co-ordination sphere is a distorted P.B. with two chlorines [Cl(1), Cl(2)] in axial positions. Atoms in the girdle follow the sequence: Cl(3), N, S, S, N; thus the molecule approximates to *m* symmetry, the mirror plane passing through the metal atom and the three chlorine atoms. This arrangement of two bidentate ligands in a plane with the *N*-methyl groups mutually *cis* is also found in two other structures in which insertion into a M-Me bond has taken place: MeTaCl<sub>2</sub>(MeN<sub>2</sub>O<sub>2</sub>)<sub>2</sub> (ref. 6) and WMe<sub>4</sub>(MeN<sub>2</sub>O<sub>2</sub>)<sub>2</sub>.<sup>15</sup>

The two axial Nb-Cl bonds [2.359(6) and 2.338(6) Å] are significantly shorter than the equatorial Nb-Cl(3) bond [2.416(5) Å]. This is a characteristic feature of the P.B. and is presumably due to the lesser ligand-ligand repulsions for atoms in axial positions, as in<sup>16</sup> *e.g.* Zr(acac)<sub>3</sub>Cl (acac = acetylacetonate) where Zr-O(ax.) is *ca.* 0.06 Å shorter than the Zr-O(eq.) bonds. The Nb-Cl(ax.) bonds in (I) are only slightly longer than those<sup>17,18</sup> in octahedral NbCl<sub>5</sub>·POCl<sub>3</sub> (2.25–2.35 Å) and NbCl<sub>6</sub><sup>-</sup> (2.29–2.37 Å), but shorter<sup>19</sup> than the mutually *trans*-Nb-Cl bonds (2.43 and 2.46 Å) in octahedral dichloro-oxo-(2,2'-bipyridyl)ethoxoniobium(v). In the girdle, the Nb-Cl(3) [2.416(5) Å] and Nb-S(1) bonds † [2.526(5) and 2.540(4) Å] are slightly shorter than those

\* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue. (Items less than 10 pp. are sent as full-size copies.)

† Where two dimensions are given, the first pertains to ligand (A) and the second to ligand (B).

<sup>15</sup> S. F. Fletcher, A. Shortland, A. C. Skapski, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1972, 922.

<sup>16</sup> R. B. Van Dreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, 1971, **93**, 2887.

found<sup>20</sup> in the P.B. girdle of NbCl(OMe)<sub>2</sub>(dedtc)<sub>2</sub> (dedtc = diethyldithiocarbamate) (2.46; 2.56, 2.56, 2.59, and 2.56 Å). There is insufficient data on Nb-N bond lengths to warrant comparisons.

In the pentagonal girdle of an ideal P.B., the angle subtended at the metal by pairs of atoms (L) is 72°. A consequence of this is close ligand-ligand contacts which restrict the size and bulk of ligands which can occupy such sites. Nevertheless, it is confirmed by X-ray results that relatively large atoms can fit into this girdle with M-L bond lengths not much greater than are found in octahedral structures. Most examples, however, such as three chlorine and two arsenic atoms,<sup>8</sup> one bromine and four sulphur atoms,<sup>20</sup> and five sulphur atoms<sup>21</sup> involve one or more bidentate ligands. There are thus precedents for atoms the size of the present five fitting in the girdle. Of additional importance in the stability of a girdle is the nature of the groups bonded to the donor atoms particularly when, as in (I), these groups (here *N*-methyl) are coplanar with the girdle.

The structure of (I) shows that these differing forces are contained, without much distortion, in a P.B. The chelate bites N(1)···S(1) are 2.51 and 2.50 Å [64.0(4) and 62.8(4)°] values considerably less than are subtended by chelating dithiocarbamates<sup>20,21</sup> which are *ca.* 68°. The S(1)···S(1) contact, 2.98 Å [72.0(2)°], is equivalent to that between sulphur atoms belonging to different dithiocarbamates.<sup>20-22</sup> The smallness of the chelate bite enables the Cl(3)-Nb-N(1) angle to expand from the ideal 72° to 80.4(4) and 82.0(4)° [2.96, 3.05 Å] thereby increasing the Cl(3)···C(2) contacts while maintaining an approximately planar girdle.

TABLE 4

Least-squares planes. Equations of planes in the form:  $Ax + By + Cz = D$ , where  $x, y, z$  are the crystallographic fractional co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

	A	B	C	D
Plane (1):				
Atoms Nb, Cl(3), S(1A), S(1B), N(1A), N(1B)	-6.61	-5.65	6.83	-1.50
[Nb 0.00, Cl(3) 0.15, S(1A) 0.05, S(1B) 0.07, N(1A) -0.14, N(1B) -0.15, C(1A) -0.12, C(2A) -0.38, C(3A) -0.26, C(1B) -0.04, C(2B) -0.40, C(3B) -0.11]				
Plane (2):				
Nb, S(1A), C(1A), N(1A)	-6.32	-5.93	7.31	-1.35
[Nb -0.01, S(1A) 0.01, C(1A) -0.01, N(1A) 0.01, C(2A) -0.10, C(3A) -0.08]				
Plane (3):				
Nb, S(1B), C(1B), N(1B)	-6.63	-3.92	7.17	-1.24
[Nb 0.01, S(1B) -0.01, C(1B) 0.02, N(1B) -0.02, C(2B) -0.14, C(3B) -0.01]				

<sup>17</sup> C. I. Branden and I. Lindqvist, *Acta Chem. Scand.*, 1961, **17**, 353.

<sup>18</sup> H. Preiss, *Z. anorg. Chem.*, 1971, **380**, 56.

<sup>19</sup> B. Kamener and C. K. Prout, *J. Chem. Soc. (A)*, 1970, 2379.

<sup>20</sup> J. W. Moncrief, D. C. Pantaleo, and N. E. Smith, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 255.

<sup>21</sup> T. F. Brennan and I. Bernal, *Chem. Comm.*, 1970, 138.

<sup>22</sup> M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *J.C.S. Dalton*, 1972, 1052.

The maximum deviation of a contributing atom from the least-squares plane (1) (Table 4) is 0.15 Å. However, Cl(3) is 0.15 Å one side of the plane while N(1A) and N(1B) are 0.14 and 0.15 Å the other side. Consequently, the dihedral angles Cl(3)-Nb-N(1)-C(2) are increased to 13.7 and 13.6°. The Cl(3)···C(2) contacts are also increased by the expansion of the Nb-N(1)-C(2) angles to 136.6(13) and 130.8(10)°.\* This significant difference in angle (in ring A > in ring B), combined with the difference in Cl(3)-Nb-N(1) angle (in ring A < in ring B) results in equivalent Cl(3)···C(2) distances of 3.18, 3.17 Å for A and B respectively. All Cl(ax.)-Nb-L(eq.) angles are within 5° of 90°. The two Nb-N(1) bonds are bent towards Cl(2) with N(1)···Cl(2) contacts of 3.10 and 3.10 Å. The two Nb-S(1) bonds and the

complexes containing three halogen atoms. They have considerable similarities, having *m* symmetry with all halogens occupying the least-crowded sites in the particular polyhedron and with all Cl-M-Cl angles at least 90°. However, the small chelate bites rule out the C.O. structure for (I); the P.B. structure is similarly ruled out by  $\pi$  bonding considerations,<sup>9</sup> bulky ligands (no unidentate PR<sub>3</sub> group has as yet been located in a P.B. girdle),<sup>10,11</sup> and multiply bonded oxygen<sup>8</sup> for the other molecules.

The two four-membered rings are closely planar (mean deviation of an atom from the plane 0.01, 0.02 Å). Atoms C(2) and C(3) are only slightly displaced from these planes (maximum 0.14 Å). Despite the proximity of the two methyl groups [C(2)···C(3) 2.95 and 3.03 Å],

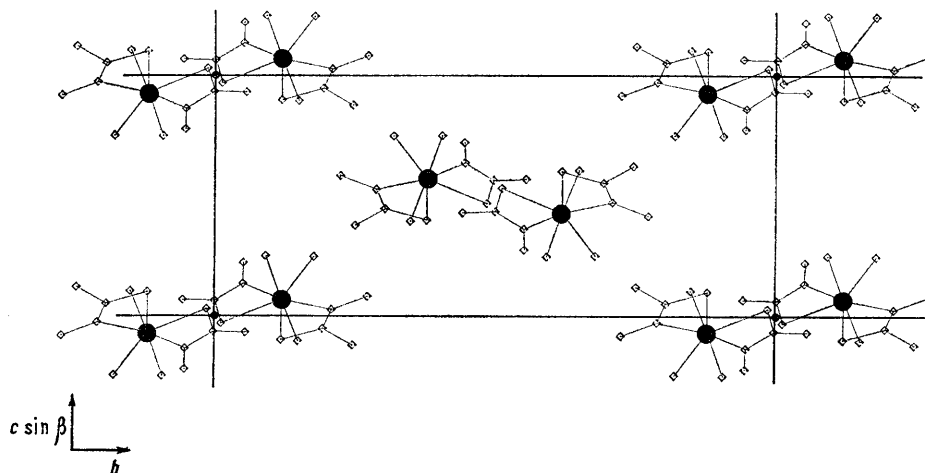


FIGURE 2 Unit cell in the *a* projection

Nb-Cl(3) bond are all bent towards Cl(1) with S(1)···Cl(1) contacts of 3.42 and 3.39 Å and a Cl(3)···Cl(1) contact of 3.29 Å.

Since the deviations from an ideal P.B. are remarkably small, the ability of this polyhedron to accommodate a wide variety of ligands without severe distortion is once more emphasised. This geometry must be favoured over the others by a sufficiently large energy difference to allow for the size of the Cl(3)···C(2) repulsions. In the other polyhedra (C.O., C.T.P.), there are arrangements of the ligands, as can be seen from models, such that the Cl···Me contacts (assuming Cl and N mutually *cis*) are larger by *ca.* 0.5 Å than in (I). Thus while (I) is well suited to a P.B., neither this structure nor those<sup>8-11</sup> which also contain three or more halogen atoms, enable us to predict the relative steric stabilities of this P.B. and the C.O. geometry with three halogen atoms in the uncapped face, although these two geometries would appear to be the most likely for seven-co-ordinate

the dihedral angles C(2)-N(1)-C(1)-C(3) are close to zero (2.7 and -2.0°). The values of the S(1)-C(1) and C(1)-N(1) bonds [1.748(16) and 1.721(19); 1.330(25)

TABLE 5

Intermolecular distances < 3.75 Å

C(3A)···Cl(2 <sup>I</sup> )	3.73	Cl(3)···C(3B <sup>III</sup> )	3.66
S(1A)···S(1A <sup>II</sup> )	3.73	Cl(3)···C(2B <sup>IV</sup> )	3.72
S(1A)···S(1B <sup>II</sup> )	3.70	C(2B)···C(1B <sup>IV</sup> )	3.74
Cl(2)···C(3B <sup>III</sup> )	3.41	C(2B)···C(3B <sup>IV</sup> )	3.67

Roman numerals as superscripts refer to atoms in the following equivalent positions, relative to the reference molecule at *x, y, z*:

$$\begin{array}{ll} \text{I} & 1 - x, -y, -z \\ \text{II} & -x, -y, -z \end{array} \quad \begin{array}{ll} \text{III} & 1 + x, \frac{1}{2} - y, \frac{1}{2} + z \\ \text{IV} & x, \frac{1}{2} - y, \frac{1}{2} + z \end{array}$$

and 1.273(20) Å] are between the single- and double-bond values<sup>23</sup> (C-S 1.81 and 1.61; C-N 1.51 and 1.29 Å) with the C-N exhibiting more double-bond character than the C-S bonds. These distances are comparable with those<sup>24</sup> in MeC(:S)NH<sub>2</sub> (1.731 and 1.324 Å), showing that the chelate ring in (I) has little or no quasi-aromatic character. The very small Nb-S(1)-C(1) angles [81.4(7) and 80.6(6)°] are far smaller than in the dithiocarbamates<sup>22</sup> (*ca.* 88 and 90°), probably for steric reasons in that a long Nb-S(1) and small

\* These differences between equivalent dimensions in the two rings are definitely significant. There are other deviations (see Table 3) which might be significant or alternatively be due to the (considerable) inadequacies of the data. A molecule of *m* symmetry is however unlikely as deviations will increase L···L contacts, *cf.* S(1)···S(1) in (I). A similar effect is found in Zr(acac)<sub>3</sub>Cl.<sup>10</sup> In addition, intramolecular forces may affect the molecular dimensions.

<sup>23</sup> L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1961, Ithaca, New York.

<sup>24</sup> M. R. Truter, *J. Chem. Soc.*, 1960, 997.

S(1)-Nb-N(1) bite can thereby be maintained in a planar ring. The Nb...C(1) distances are 2.85 and 2.82 Å. The small Nb-S(1)-C(1) angles contrast with the Nb-N(1)-C(1) angles of 105.7 and 104.1°. The S(1)-C(1)-N(1) angles are 108.8 and 112.4°, *cf.* 117.7° in ref. 24, and considerably smaller than the other angles subtended at C(1).

Figure 2 is a packing diagram in the *a* projection. Intermolecular contacts are confined to the normal van der Waals contacts and Table 5 lists those <3.75 Å.

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